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OLI Corrosion Modeling Basics

using OLI Studio: Corrosion Analyzer

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Agenda

1. Introduction to OLI Studio:
   Stream Analyzer and Corrosion Analyzer
2. Introduction to the **OLI Corrosion Model**
3. Seawater Corrosion
   Material Selection
4. Pourbaix Diagrams
   Au-H2O and Fe-H2O systems
5. Effect of Inorganic Inhibitors on Corrosion Rates
6. Q&A Section

OLI systems, inc.

OLI Studio

Stream Analyzer

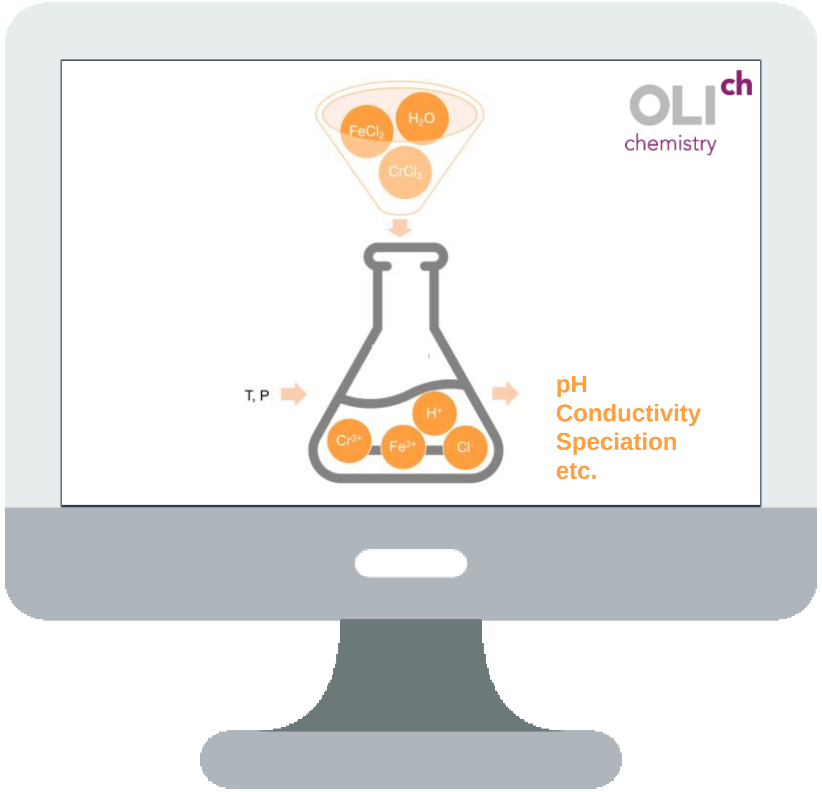
Corrosion Analyzer

ScaleChem

OLI Studio: Stream Analyzer Overview

Stream Analyzer is a comprehensive thermodynamic tool that calculates:

Speciation, Phase equilibria, Enthalpies, Heat capacities, Densities, etc., in mixed-solvent multicomponent systems



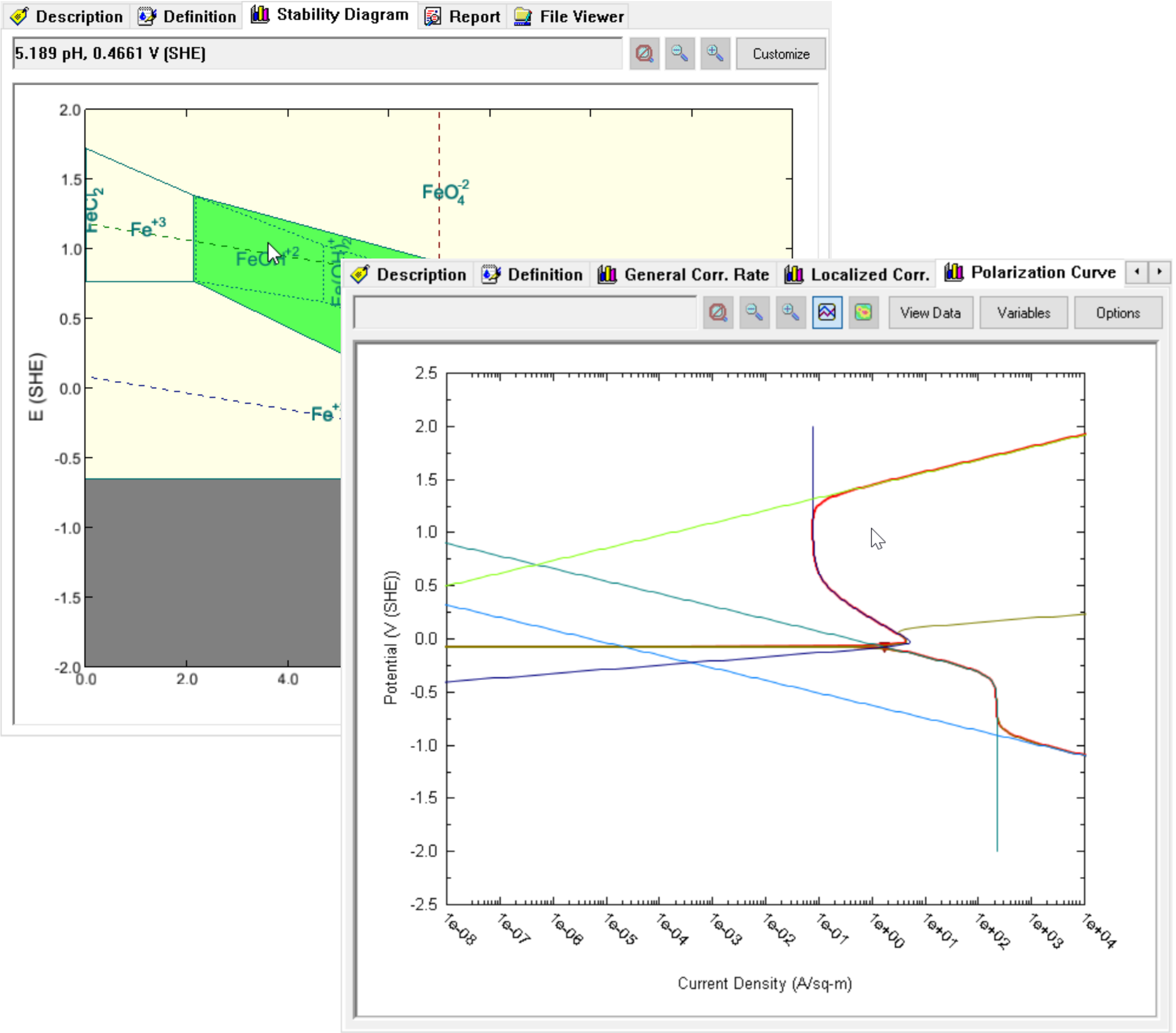
Capabilities and features of Stream Analyzer include:

- **Three different thermodynamic frameworks:**
  - Aqueous (AQ) model
  - Mixed Solvent Electrolyte (MSE) model
  - Mixed Solvent Electrolyte and Soave-Redlich-Kwong (MSE-SRK) model
- **Thermophysical properties:** Stream Analyzer has thermophysical models to predict surface tension, interfacial tension, viscosity, electrical conductivity, thermal conductivity, diffusivity, and osmotic pressure.
- **Molecular and ionic inflows:** Stream Analyzer accepts molecular inflows typical of a process stream; and ion inflows typical of a sample water analysis.

OLI Studio: Corrosion Analyzer Overview

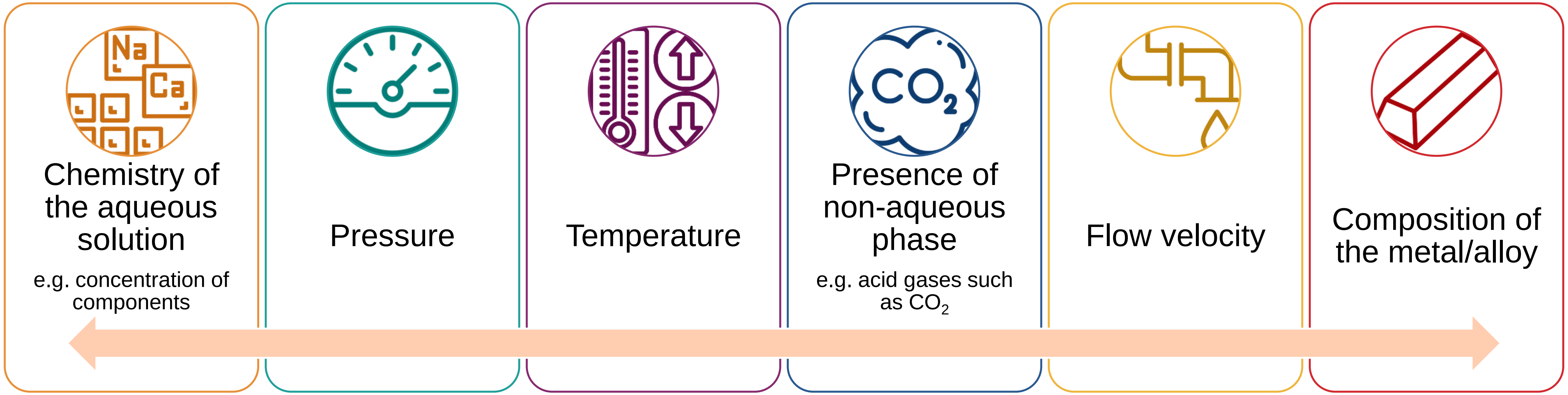
Capabilities and features of Corrosion Analyzer are:

- ✓ Calculation of **general corrosion** rates
- ✓ **Localized corrosion** susceptibility – *calculating the worst-case pitting rate*
- ✓ Generation of **polarization curves** plots
- ✓ Generation of **Pourbaix (E vs pH) diagrams**
- ✓ Heat treatment effect



Introduction to the OLI Corrosion Model

Corrosion rates in aqueous environments depend on multiple factors, such as:



To get an understanding of each one of these factors, or a combination of these factors, computational modeling is **advantageous**.

The strength of the OLI corrosion model is the ability to provide a realistic representation of **chemical equilibria** and **thermophysical properties** in the bulk solution, and at the same time, to account for the phenomena at the **metal-solution interface**.

Introduction to the OLI Corrosion Model

Thermophysical module

- Computes **the speciation** of species in aqueous solutions, e.g. $CO_2 + H_2O \rightarrow H^+ + HCO_3^-$
- Calculates the **concentrations** and **activities** of ionic species and neutral species in aqueous solutions
- Calculates **transport properties** of individual species, such as viscosity and diffusivity, to predict mass-transfer effects

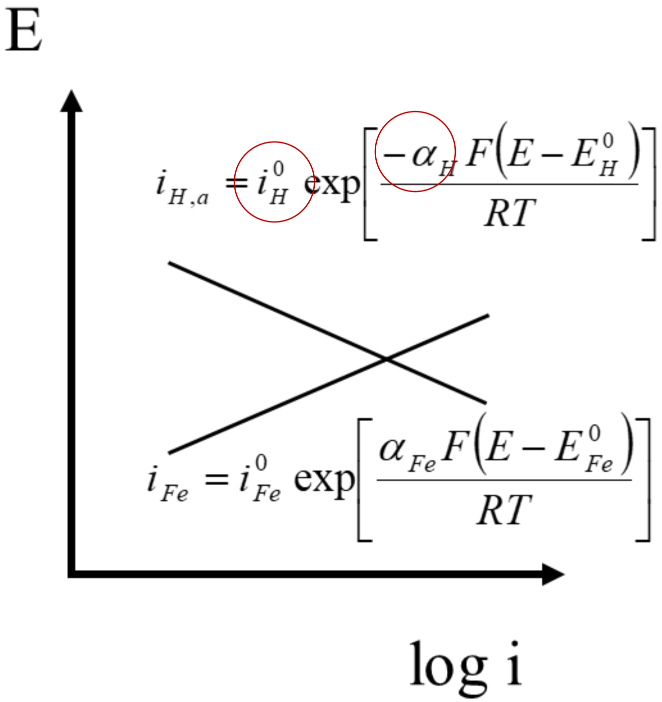
Thermodynamic Framework
Aqueous **(AQ)*** model

Electrochemical module

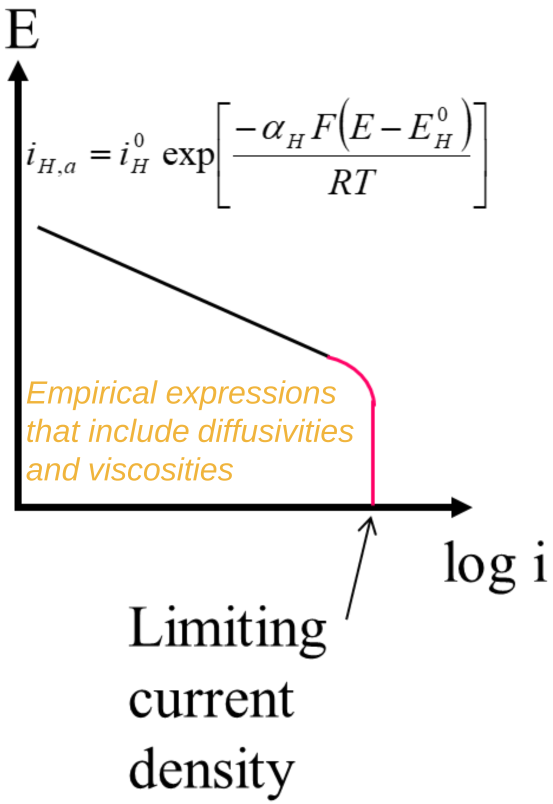
- Simulates partial **oxidation** and **reduction** processes on the surface of the metal
- Reproduce the **active-to-passive** transition and effect of solution species on passivity
- Reproduce **experimental corrosion rates** using parameters calibrated using experimental data
- The prediction of corrosion potential and corrosion rates involves 3 aspects of **Corrosion Kinetics**:
  - Chemical Kinetics – **Activation control model**
  - Mass Transfer – **Diffusion control model**
  - Passivity - **Fraction surface coverage model**

Prediction of corrosion rates

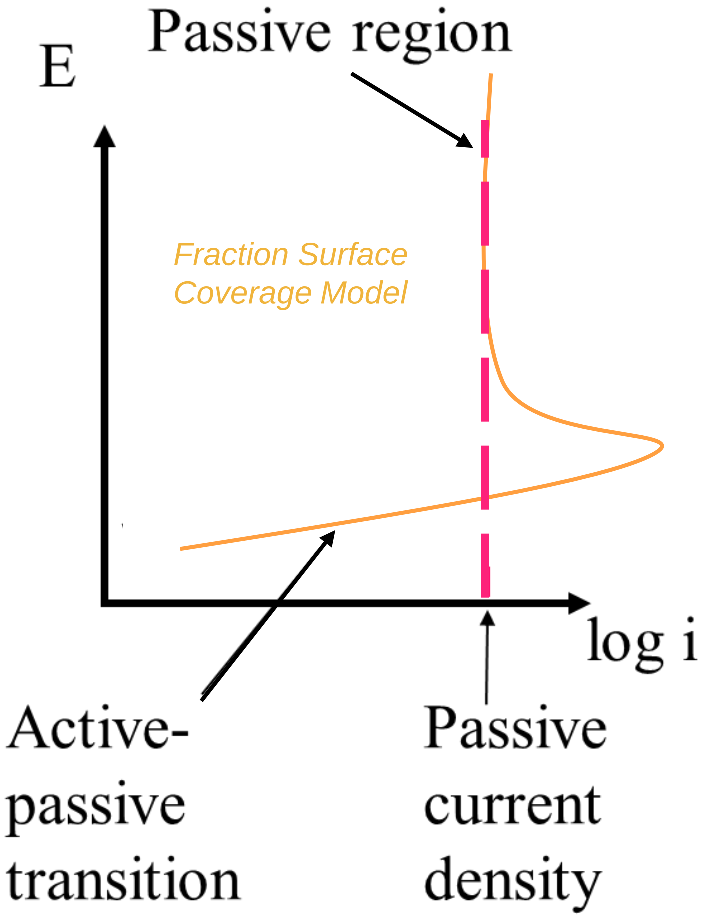
1. Activation Control



2. Diffusion Control



3. Passivity



Corrosion in Seawater

- **Chlorides** and **oxygen** in sea water can attack the films that passivate the steels.

- The **Corrosion Analyzer** will be used to:

    - Enter ionic inputs
    - Model the effects of chlorides and oxygen on the rates of uniform corrosion, and the propensity of pitting (localized corrosion)

1. Adding a Water Analysis

- Add a Water Analysis - Add Water Analysis
  - Rename it *Seawater*
- Select the **AQ** Framework
- **Add a water analysis** given in the table to the right
- Go to the **Add Reconciliation** button
  - Rename it *Deaerated Seawater*
- Select **Reconcile pH**
- Click **Calculate**
- Go to the **Report** tab

Deaerated seawater composition

Species	**Concentration (mg/L)**
Cl^-	19000
Na^+	10700
Mg^{+2}	1300
Ca^{+2}	400
SO_4^{-2}	2750
HCO_3^-	150

Conditions

pH	8.0
Temperature	25 ^oC
Pressure	1 atm

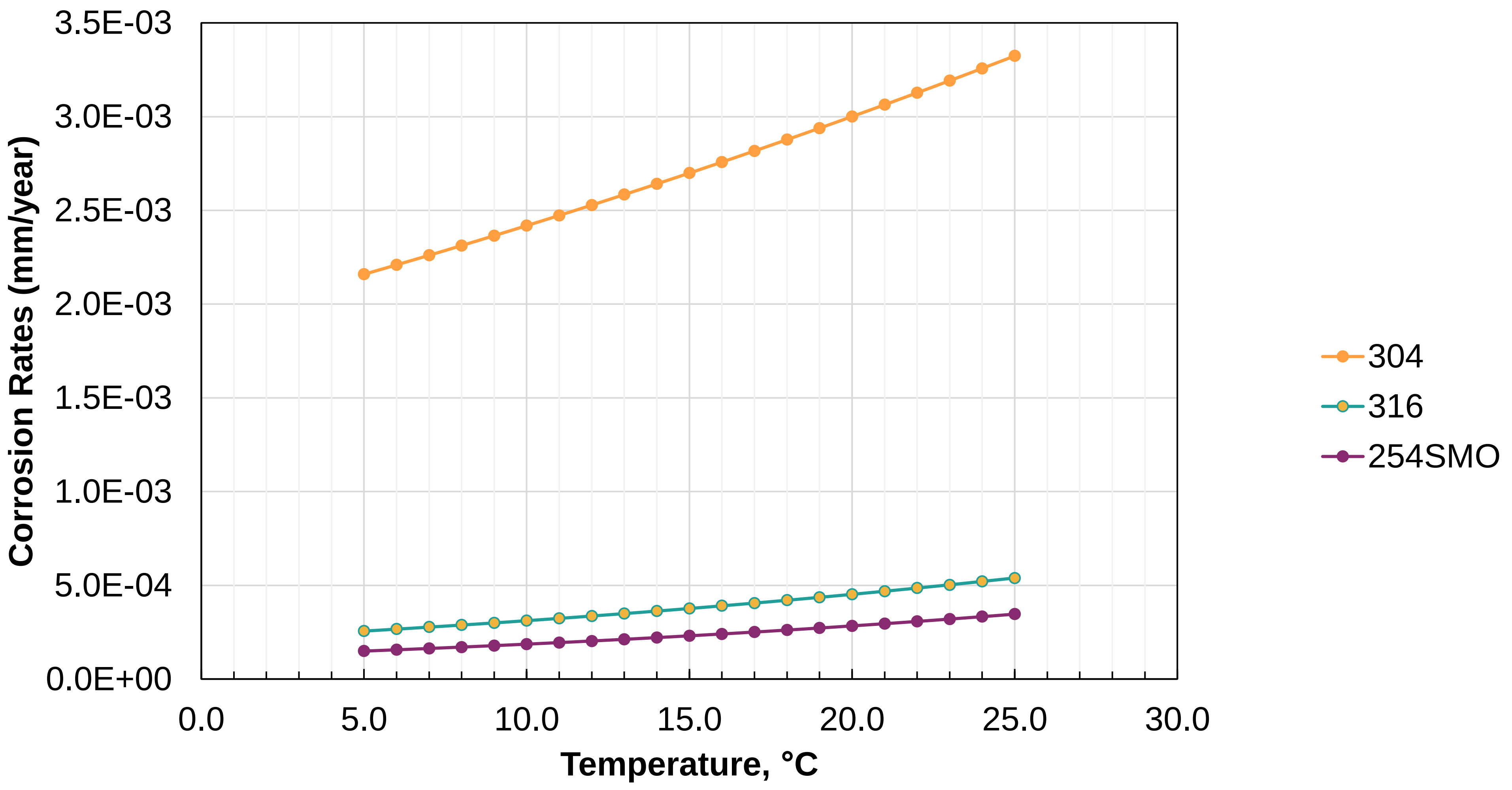
2. Corrosion Rate Calculation

Corrosion of 304, 316 and 254SMO alloys in a **Deaerated** Seawater Solution

- Select the **Molecular Deaerated Seawater**
- Change corrosion rate units to **mm/year,** voltage to **mV SCE,** and current density to **μA/cm²**
- Go to the **Add Calculation** button and select **Corrosion Rates**
  - Rename it *304SS Corrosion Rates*
- Change to survey by **Temperature**
  - Range T = 5 - 25°C by 1°C increments
- Flow Type: **Pipe flow**
  - Leave the default values for velocity and pipe diameter
- Select **Stainless Steel 304** as the **Contact Surface**
  - A drop-down arrow will show the different alloys in the database
- Click **Calculate**
- Repeat the same steps for 316 **Stainless Steel**
- Go to the **General Corrosion** tab to analyze the corrosion rates

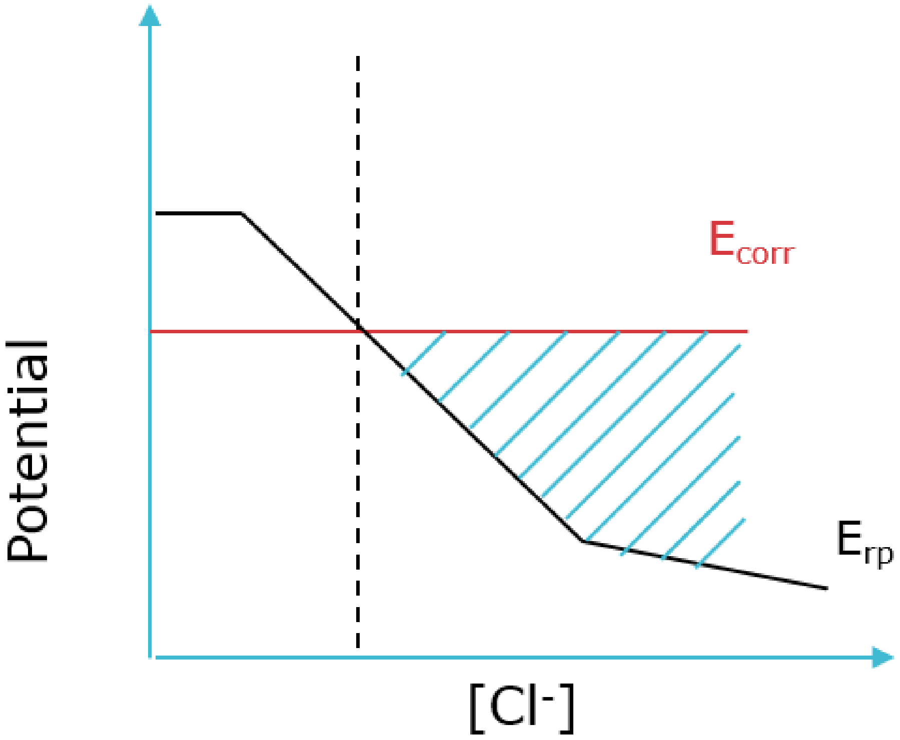
List of alloys	
Carbon Steel A212B	Ni
Carbon Steel A216	Alloy 600
Carbon Steel G10100	Alloy 690
Carbon Steel 1018	Alloy 825
Stainless Steel 304	Alloy 625
Stainless Steel 316	Alloy C-276
Alloy 254SMO	Alloy C-22
Duplex Stainless 2205	Alloy 28
Duplex Stainless 2207	Alloy 29
13%Cr Stainless Steel	Alloy 2335
Super13Cr Stainless Steel	Alloy 2550
Super15Cr Stainless Steel	Cu
Super17Cr Stainless Steel	CuNi 9010
Aluminum 1199	CuNi 7030
Aluminum 1100	

Corrosion Rates of 304, 316 and 254SMO alloys in Deaerated Sea Water as a Function of Temperature



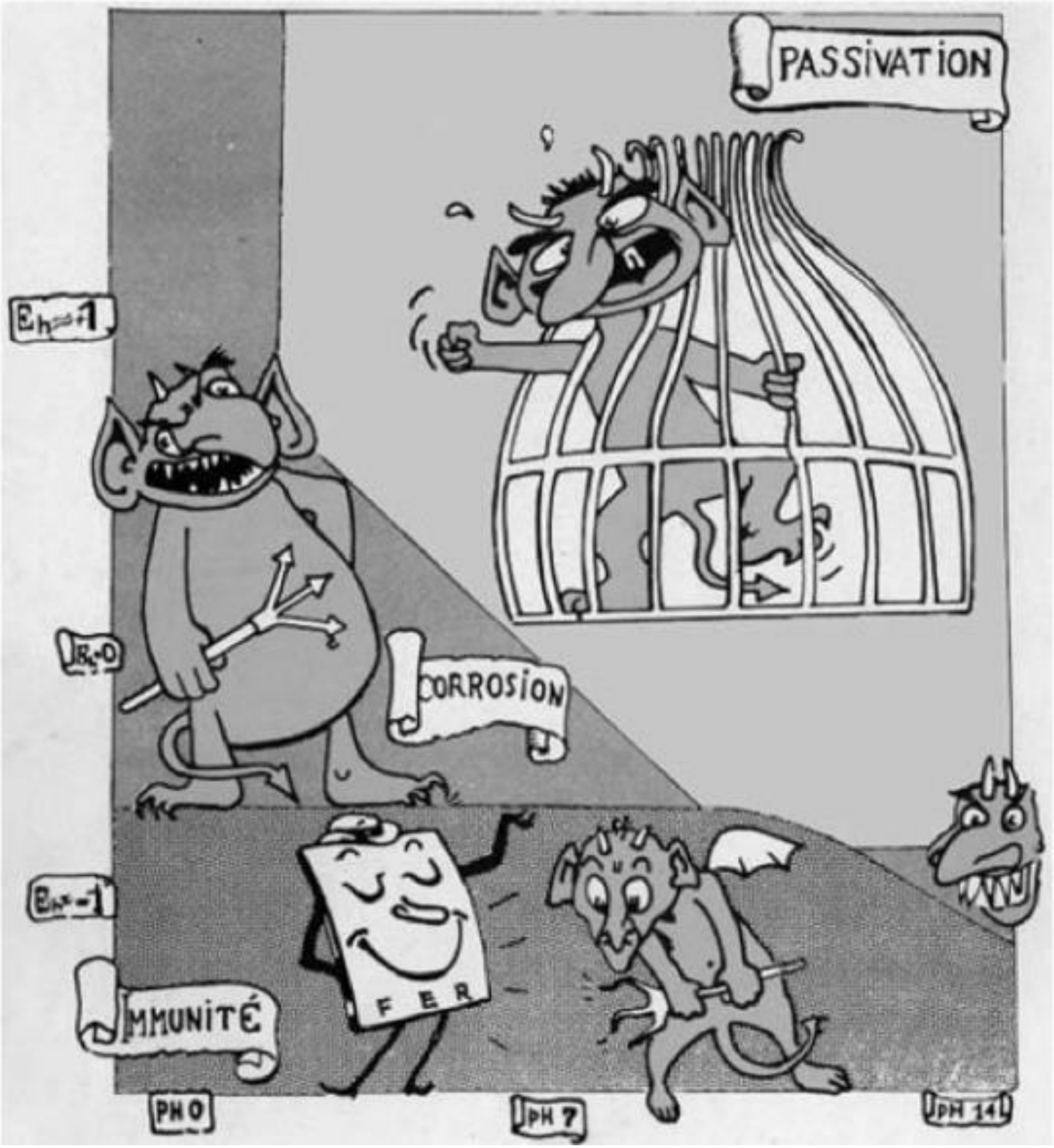
Localized Corrosion

- The shaded area represent the region where $E_{corr} > E_{rp}$
- The shaded regions also represent the conditions under which pits can form
- The wider the E_{corr}-E_{rp} difference, the greater the propensity for localized corrosion



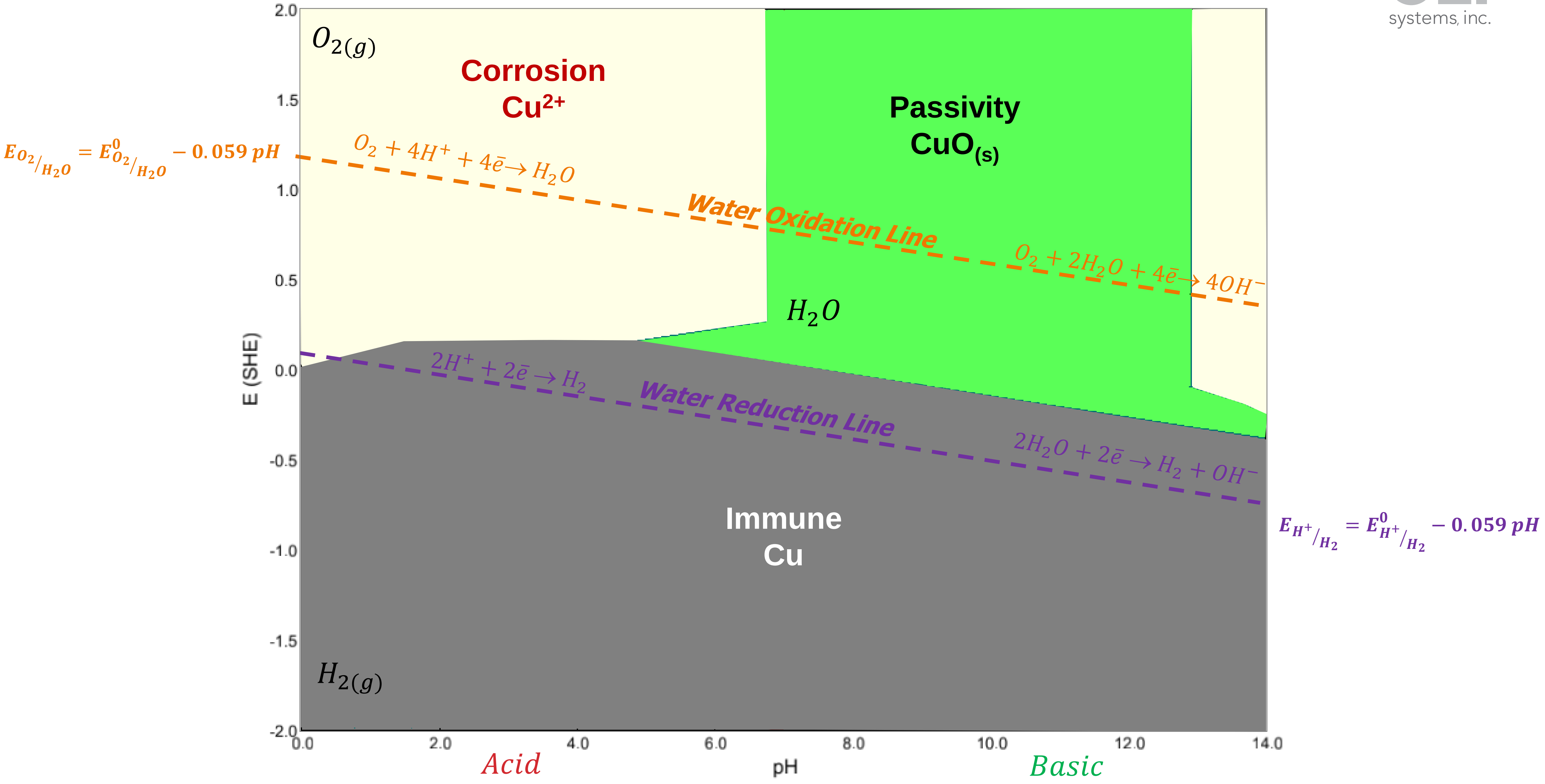
Real-solution Stability Diagrams

- Incorporates an accurate coefficient model for multicomponent systems (**AQ**, **MSE**, **MSE-SRK** thermodynamic models)
- Adds the ability to construct stability diagrams in wide range of T, P and concentrations of species
- Allows you to choose a solution component as an independent variable, so that the effect of any solution components can be studied explicitly
- Uses realistically modeled acids and bases to vary solution pH



Picture Courtesy: *Introduction to Corrosion Science by E. McCafferty*

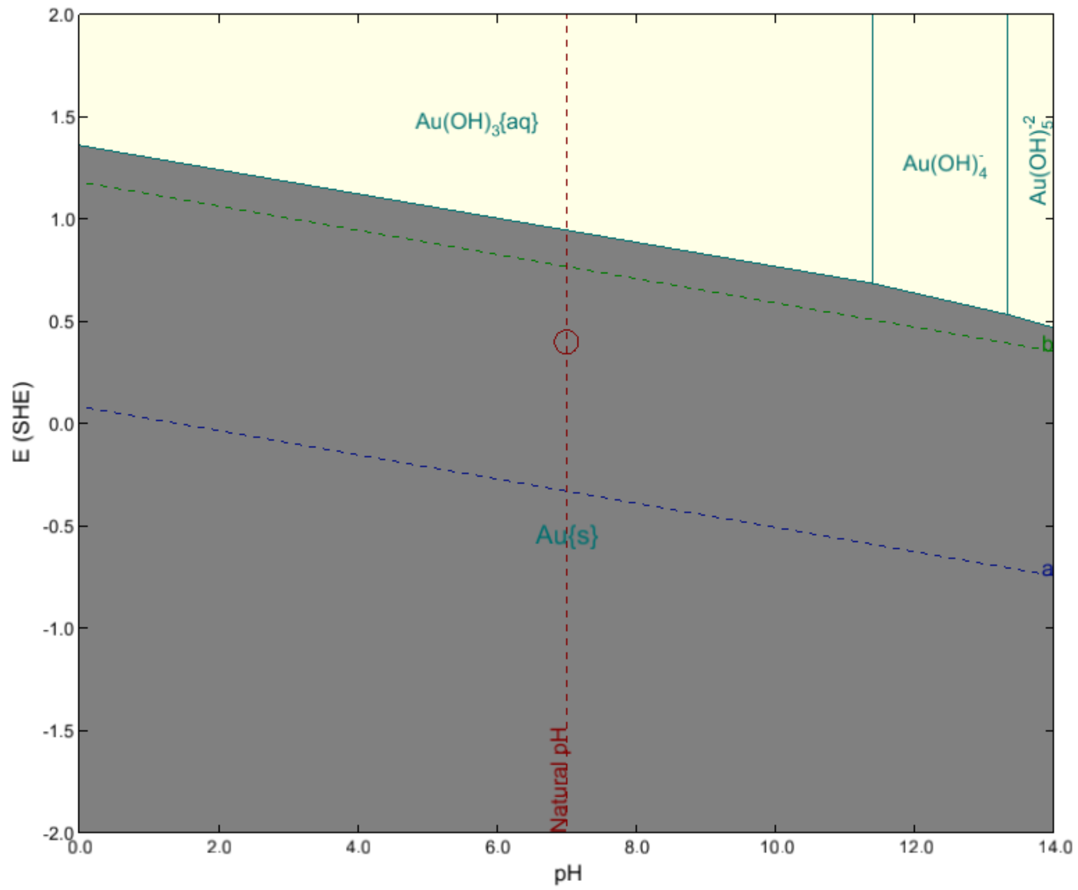
Pourbaix Diagram of Cu in H_2O at 25 ºC



Why doesn't gold corrode?

- Add a new Stream
  - Rename it ***Au Pourbaix Diagram***
- Select the AQ Framework
- Go to the **Add Calculation** button and select **Stability Diagram**
- Rename it ***Au-H2O system***
- Add **Au** as the **Contact Surface**
  - Specs: **Show ORP** and **No aqueous lines**
- Add H2SO4 as the **Acid Titrant**
- **Note:** Notice that **Re** button turns ON
- Click **Calculate**
- Go to the **Stability Diagram** tab to see the Plot

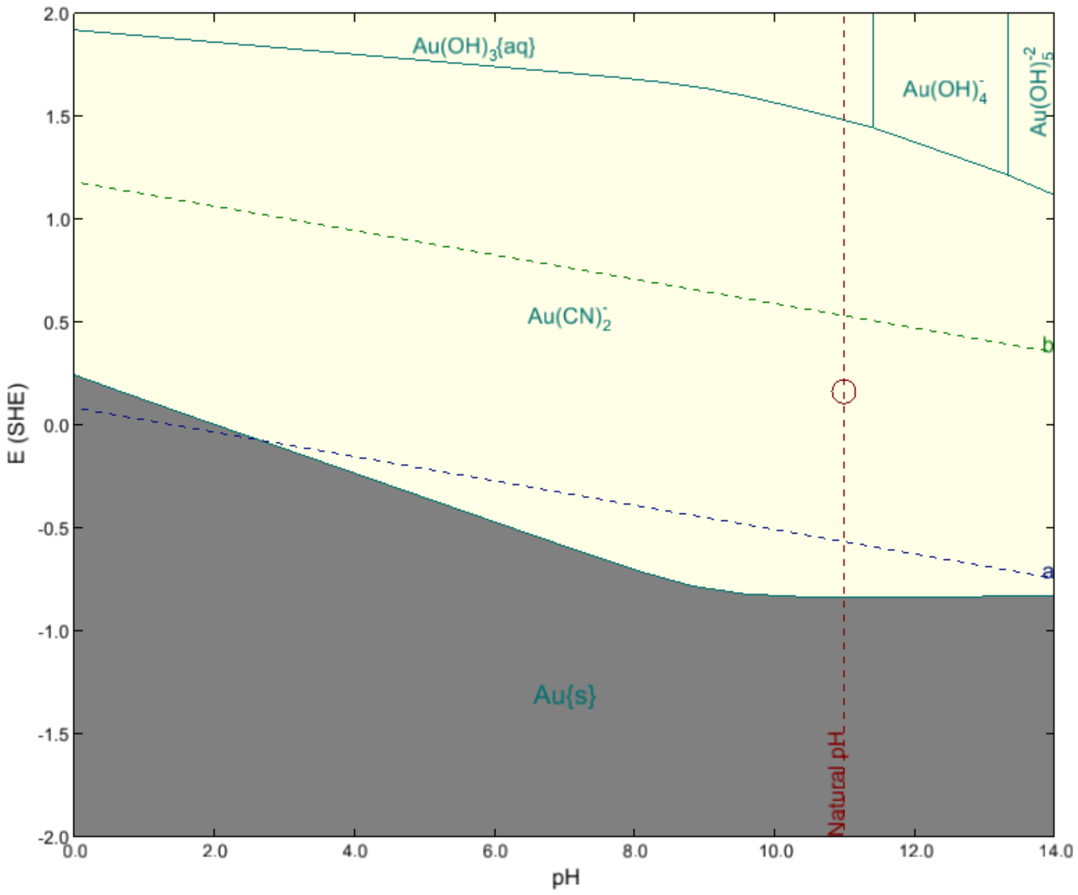
Au-H_2O system



Hydrometallurgy of Gold

Au-CN-H_2O system

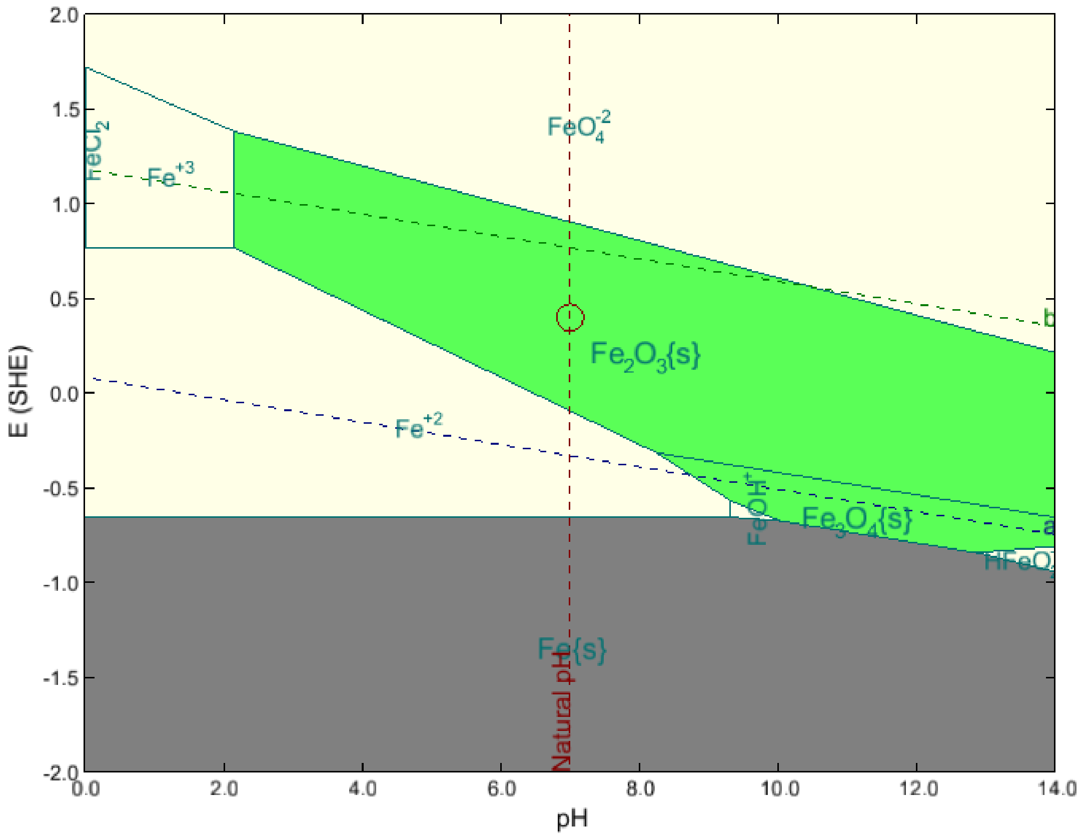
- Go to the **Add Calculation** button and select **Stability Diagram**
- Rename it ***Au-CN-H2O system***
- Add **Au** as the **Contact Surface**
  - **Customize: Show ORP** and **No aqueous lines**
- **Add** 1e-4 moles **NaCN** to the inflows
- Click **Calculate**
- Go to the **Stability Diagram** tab to see the Plot



Stability Diagram of Fe in Water

- Add a new Stream
  - Rename it ***Fe Pourbaix Diagram***
- Select the **AQ** Framework
- Go to the **Add Calculation** button and select **Stability Diagram**
- Rename it ***Fe-H2O system***
- Add Fe as the **Contact Surface**
  - Show ORP and no Aqueous lines
- Click **Calculate**
- Go to the **Stability Diagram** tab

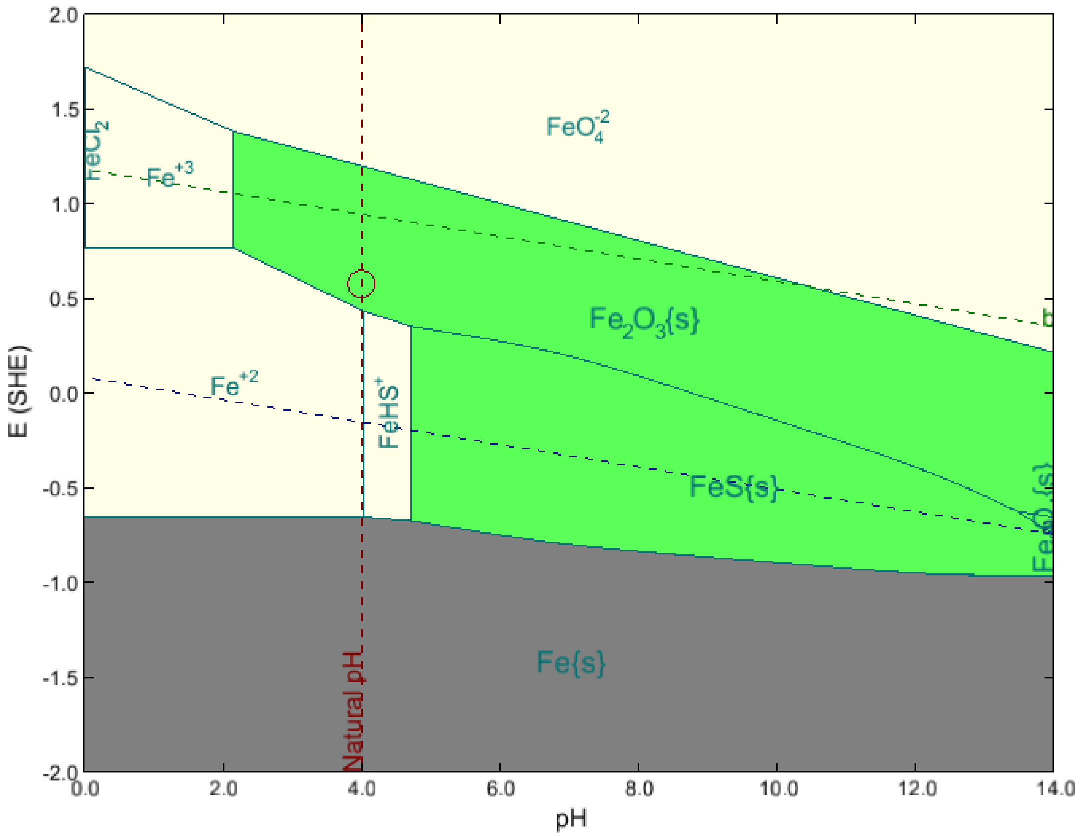
Fe-H2O system



Effect of H_2S on the Stability Diagram of Carbon Steel

- Go to **Add Calculation** button and select **Stability Diagram**
- Rename it ***Fe-H2S-H2O system***
- Add Fe as the **Contact Surface**
- **Add** 1e-4 moles of H2S
- Click **Calculate**
- Go to the **Stability Diagram** tab

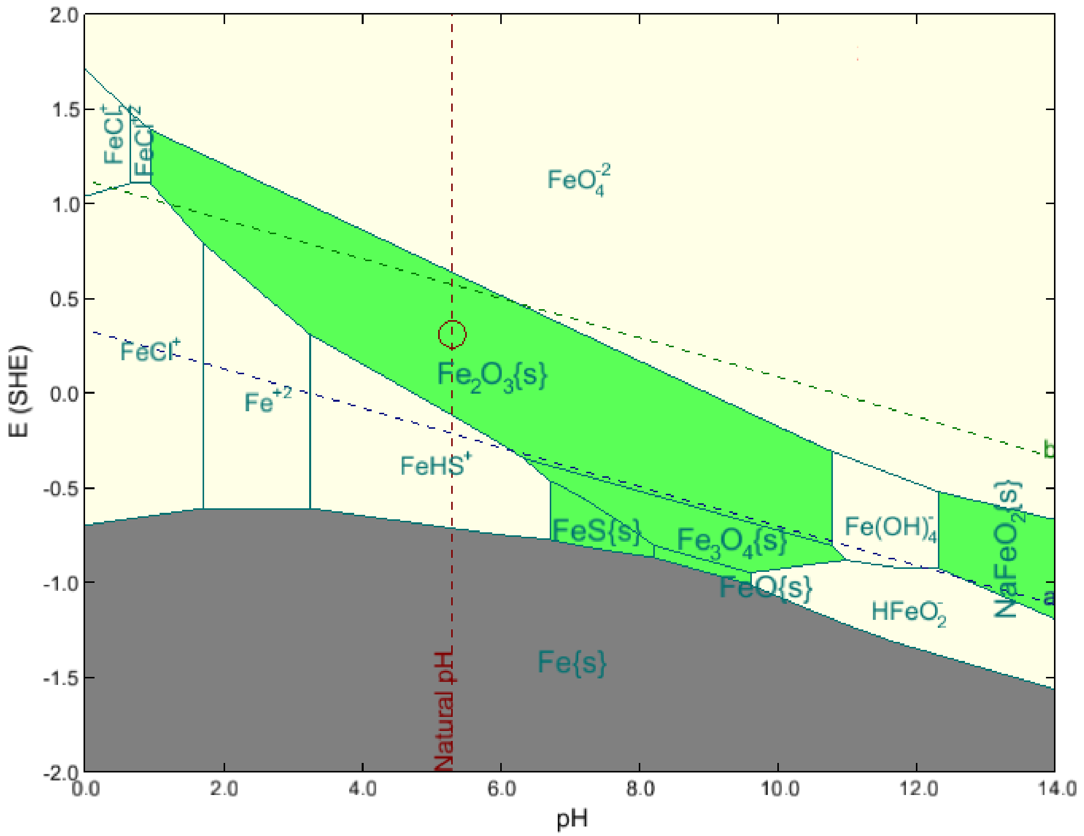
Fe-H_2S-H_2O System



Effect of H_2S and Temperature on the Stability Diagram of Carbon Steel

- Go to **Add Calculation** button and select **Stability Diagram**
- Rename it *Fe-H2S-H2O vs T system*
- Add Fe as the **Contact Surface**
- **Add** 1e-4 moles of H2S
- **Temperature** and **Pressure** conditions
  - 25°C – 1 atm
  - 80°C – 1 atm
  - 250°C – 60 atm
- Click **Calculate**
- Go to the **Stability Diagram** tab

250°C, 60 atm



Effect of Inhibitors on Corrosion Rates

- Evaluate the corrosion rates of a water storage tank made out of a **1-inch thick carbon steel 1018** containing aerated water.

- Which inhibitor should we add **to increase the tank's lifetime** by **10** more years?

Table 1. List of inhibitors studied in the OLI Corrosion Model. The corrosion model was validated with each one of these inhibitors and their effect on the decrease of the corrosion rate of Carbon Steel and some selected CRAs.

Inhibitor	Carbon Steel	CRAs
PO_4^{-3}	✓	
MoO_4^{-2}	✓	✓
NO_3^{-}	✓	✓
NO_2^{-}	✓	
CrO_2^{-4}	✓	
SiO_4^{2-}	✓	

Note: *When the concentration of Cl^- is too high the effect of these inhibitors on the reduction of corrosion rate is diminished.*

Effect of Inhibitors on Corrosion Rates

Calculating the Corrosion Rates of Carbon Steel 1018

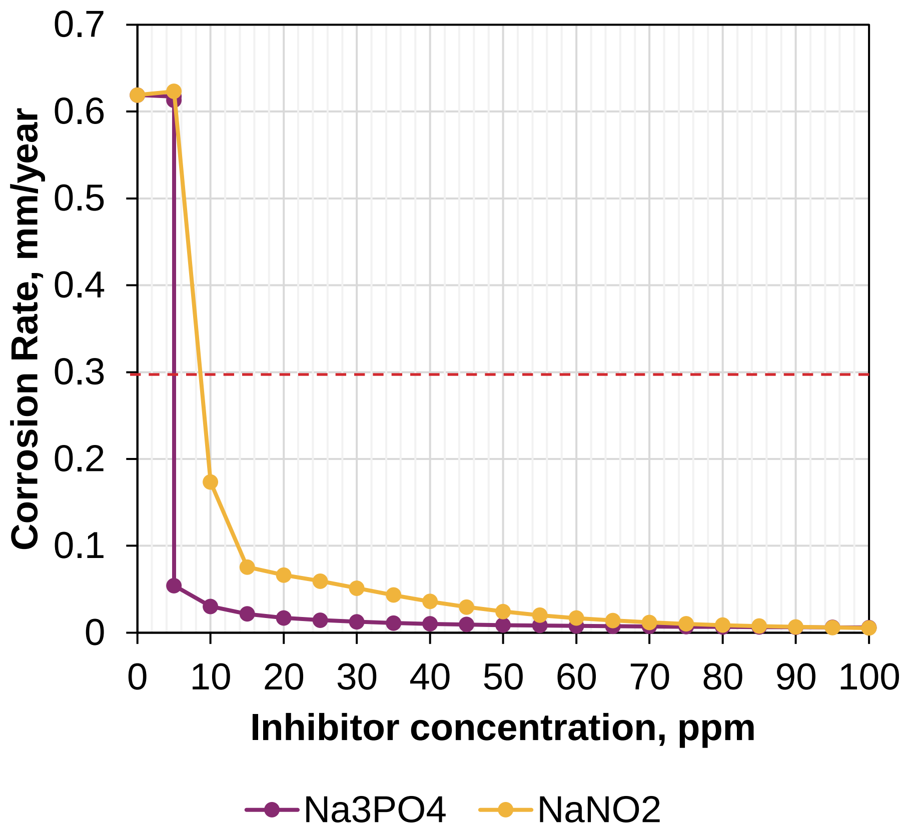
Inputs

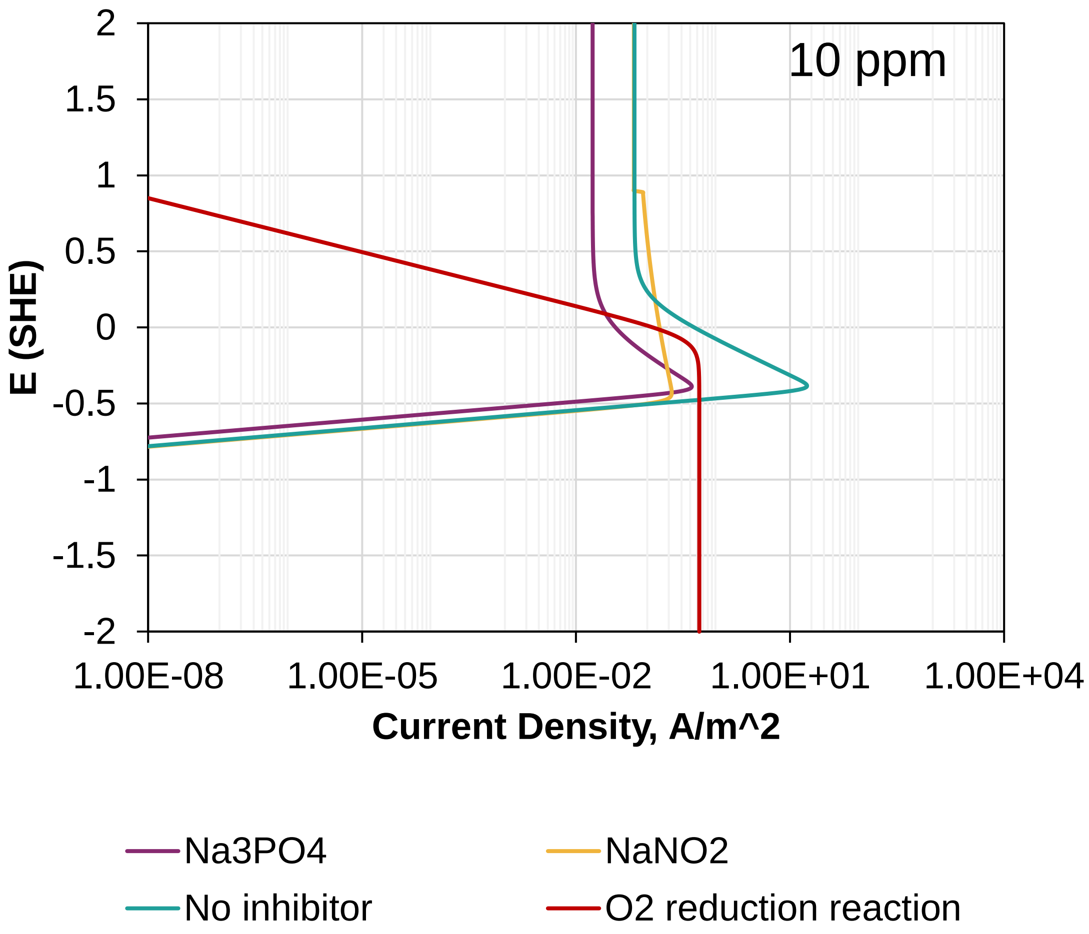
- **Temperature:** 25 ºC
- **Pressure:** 1 atm
- **Thermodynamic Framework:** Aqueous (AQ)
- **Solution:** Water saturated with oxygen
- **Inhibitors:** **Silicates and Phosphates**
- **Flow type:** Static
- **Alloy:** Carbon Steel 1018
- **Type of Calculation:** Survey by Inhibitor composition

Outputs

- **Corrosion rates** as a function of inhibitor concentration.
  - Which is the **optimal inhibitor concentration** to increase the tank's lifetime?
- Change in the anodic and cathodic reactions and their final effect on the polarization curve

Simulation Results



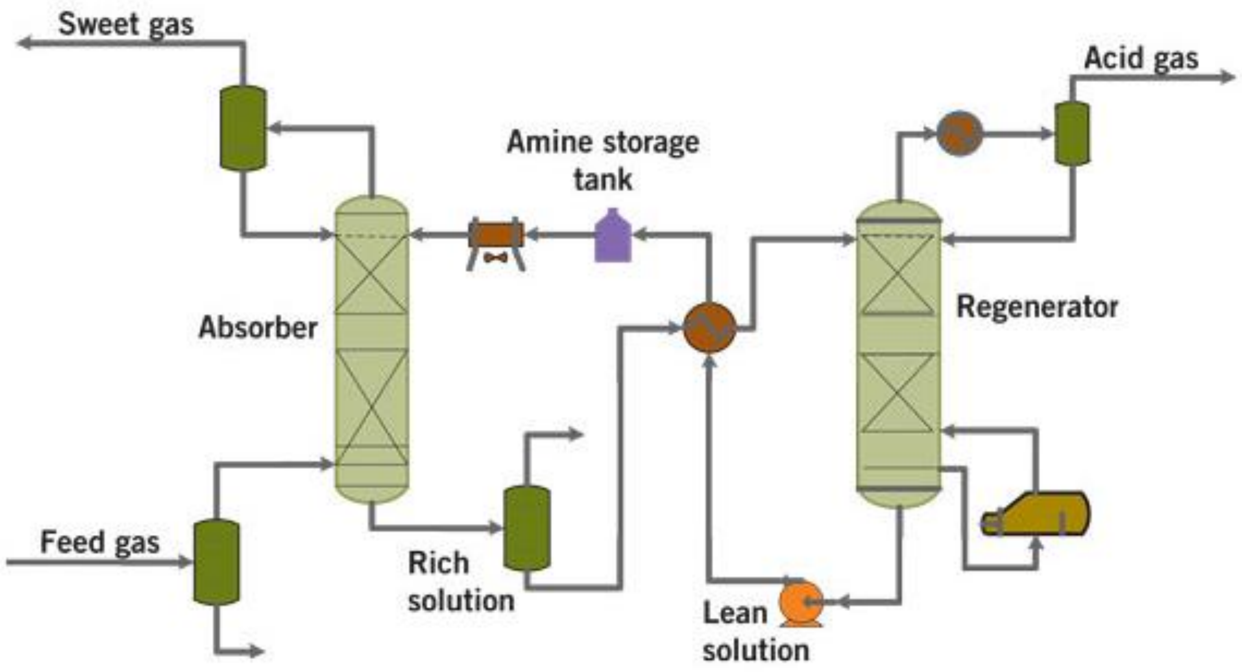


$$Life\ time = 25.4\ mm \times \frac{1\ year}{0.62\ mm} \approx 41\ years$$

$$Life\ time = 25.4\ mm \times \frac{1\ year}{0.3\ mm} \approx 85\ years$$

Gas Condensate Corrosion

- Gas condensates from alkanolamine gas sweetening plants can be highly corrosive.
- Diethanolamine is used to neutralize (sweeten) a natural gas stream. This removes carbon dioxide and hydrogen sulfide. The off gas from the regeneration is highly acidic and corrosive.
- The **Corrosion Analyzer** will be used to:
  - Enter molecular inflows
  - Determine the dew point of the acid gas
  - Remove the condensed phase and perform corrosion rate calculations



Example 26 – Corrosion Rates

Calculating the Dew Point Temperature

- Add a new Stream
  - Rename it ***Gas Condensate***
- Select the **AQ** Framework
- Change the **units** to Metric | Batch | Mole Frac.
- Add the chemistry in the table to the right
- Go to the **Add Calculation** button and select **Single Point** Calculation
  - Select Dew Point
  - Rename it ***Dew Point Temperature***
- Click **Calculate**
- Go to the **Report** tab

Conditions and composition of Acid Gas

Temperature	38 ^oC
Pressure	1.2 atm

Species	Concentration (mole %)
H_2O	5.42
CO_2	77.4
N_2	0.02
H_2S	16.6
CH4	0.50
C2H6	0.03
C3H8	0.03

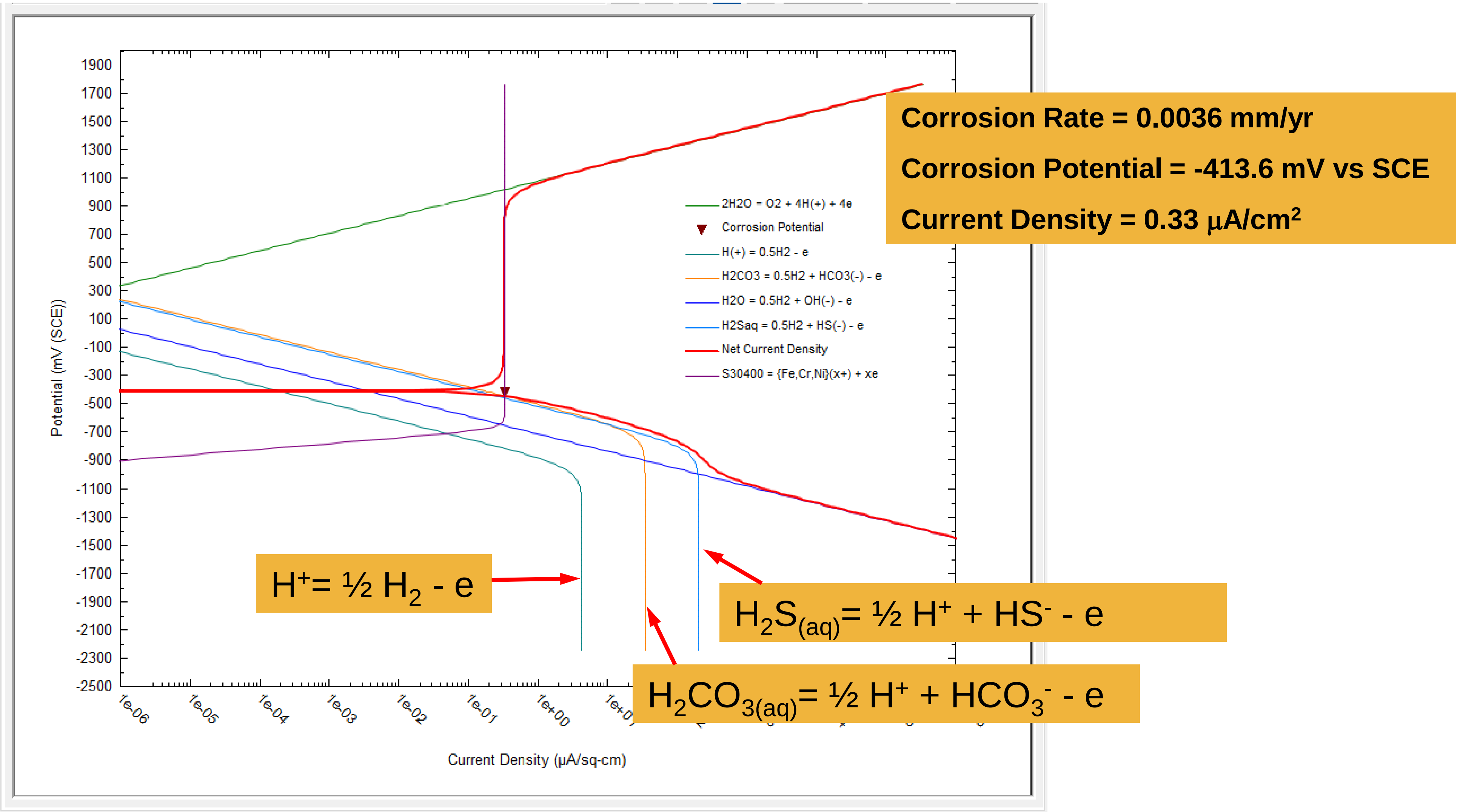
Example – Corrosion Rates

Calculating the Corrosion Rates of 304SS and 13% Cr

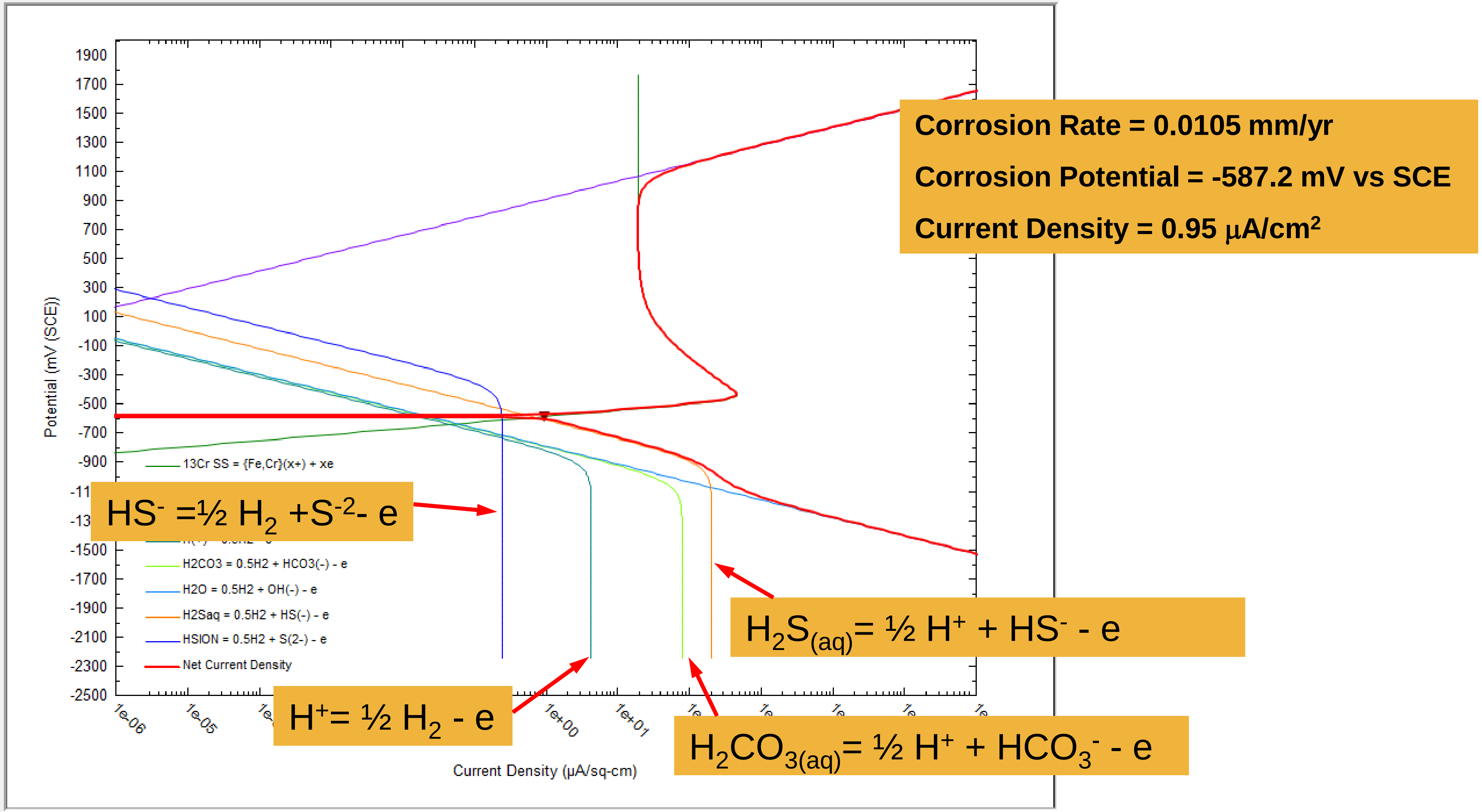
- Select the **Dew Point Temperature** Calculation
  - Add as a Stream
  - Name it: ***Corrosion – Gas Condensate***
- Go to the **Add Calculation** button and select **Corrosion Rates**
  - Select **Single Point Rate**
  - Name it: ***304SS Corrosion Rate***
- Flow Type: **Static**
- Select **Stainless Steel 304** as the **Contact Surface**
- Click **Calculate**
- Do the same for **13% Cr**
- Go to the **General Corrosion** tab and **Polarization Curve** tab

Alloy	Corrosion Rate
304SS	0.0036 mm/year
13%Cr	0.0105 mm/year

304 Stainless Steel Corrosion @ Dew Point



13 % Cr Steel Corrosion @ Dew Point



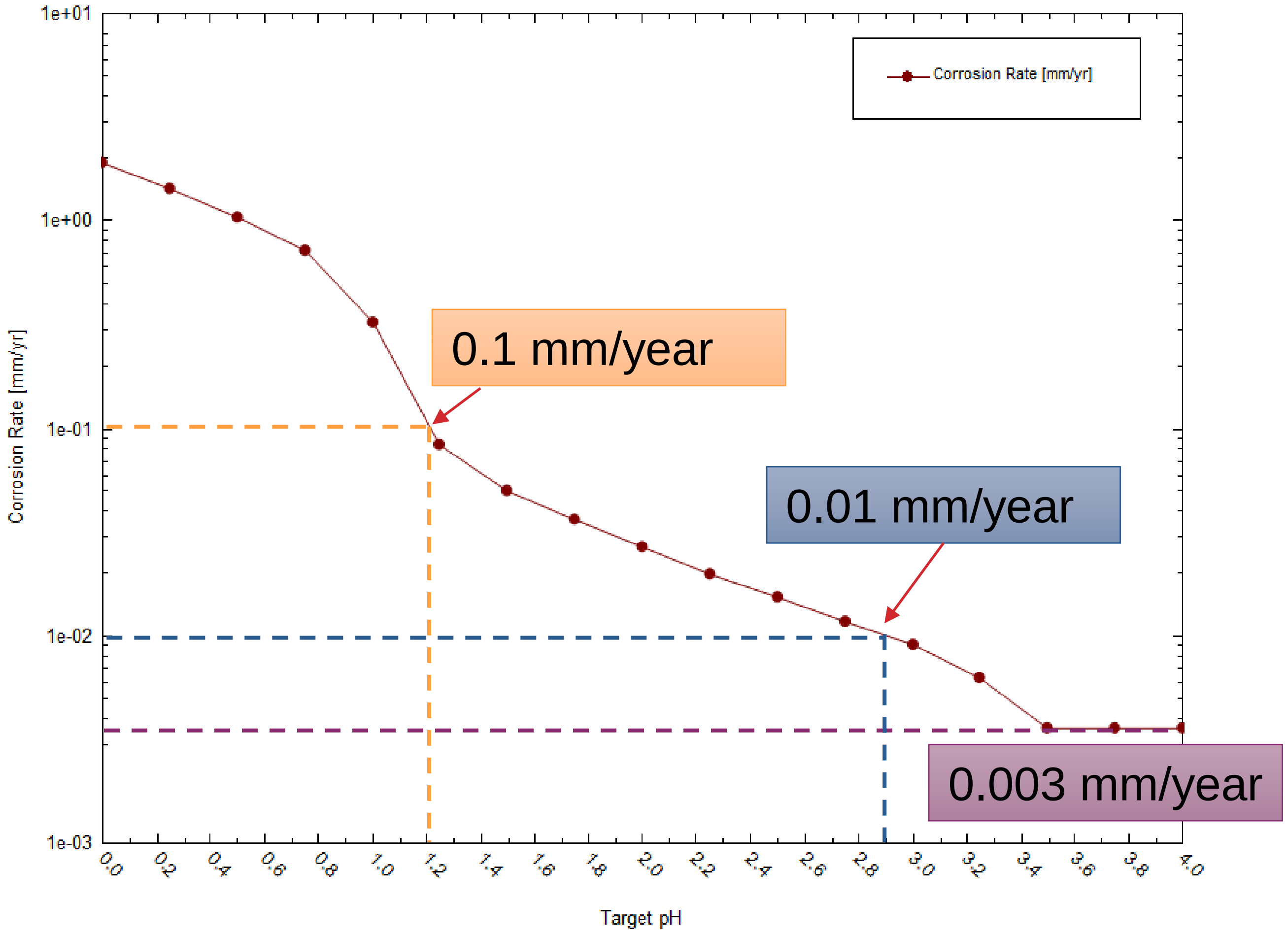
Corrosion Rate = 0.0105 mm/yr

Corrosion Potential = -587.2 mV vs SCE

Current Density = 0.95 µA/cm²

Corrosion Rates as a function of pH

- Select the **Corrosion – Gas Condensate** Stream
- Go to the **Add Calculation** button and select **Corrosion Rates**
    - Select Survey by **pH**
    - Name it: ***304SS CR vs pH***
- **pH range** = 0 - 4 every 0.25 steps
- Flow Type: **Static**
- Select **Stainless Steel 304** as the **Contact Surface**
- Click **Calculate**
- Go to the **General Corrosion** tab



Thank you!

Q&A

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