



REFERENCE GUIDE TO  
OLI Studio: Corrosion Analyzer  
V10



think simulation



getting the  
chemistry right

## Introduction to OLI Studio

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Version: OLI Studio v10

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if you need to contact Support, an online request form is located at the OLI Systems Tech Support page at <https://www.olisystems.com/contact-tech-support>. Other useful links and resources are:

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## Disclaimer

This manual was produced using the OLI Analyzer 10.0 build 1 (10.0.1). As time progresses, new data and refinements to existing data sets can result in values that you obtain being slightly different than what is presented in this manual. This is a natural progress and cannot be avoided. When large systematic changes to the software occur, this manual will be updated.

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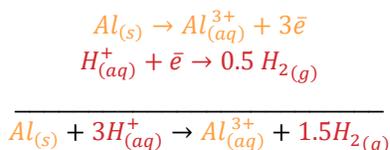
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## Chapter I – RedOx

RedOx is an OLI Studio option that activates a critical mechanism in electrolyte chemistry. All elements possess the ability to gain (reduction) or release (oxidation) electrons. When oxidation occurs, elements increase their oxidation state. When reduction occurs, the element decreases its oxidation state. The software's RedOx option allows us to modify the oxidation state of a system so that we can better represent an actual process.

We can tell there has been a transfer of electrons in a reaction if there is any change in the oxidation number between the reactants and the products.

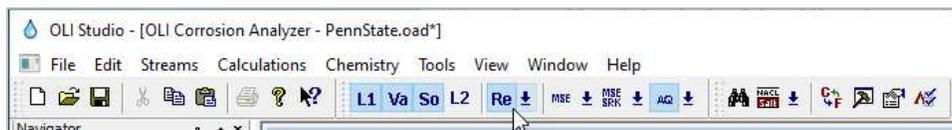
Example:



**Oxidation:** Al lost electrons

**Reduction:** H gained electrons

In the software the RedOx reactions are turned OFF by default. The software assumes that there is not RedOx happening. To enable RedOx reactions, we need to click on the **Re** button.



## Transition Metals

When the **Re** button is turned ON the software automatically turns on the oxidation and reduction reactions for the **transition metals** elements and some elements that belong to **other metals** category (see periodic table below), that are defined in the chemistry.

**Periodic table of the elements**

Legend:

- Alkali metals
- Alkaline-earth metals
- Transition metals
- Other metals
- Other nonmetals
- Halogens
- Noble gases
- Rare-earth elements (21, 39, 57-71) and lanthanoid elements (57-71 only)
- Actinoid elements

group	1*	2											13	14	15	16	17	18
1	H																	He
2	Li	Be											B	C	N	O	F	Ne
3	Na	Mg											Al	Si	P	S	Cl	Ar
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7	Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og
lanthanoid series 6			58	59	60	61	62	63	64	65	66	67	68	69	70	71		
actinoid series 7			90	91	92	93	94	95	96	97	98	99	100	101	102	103		

\*Numbering system adopted by the International Union of Pure and Applied Chemistry (IUPAC). © Encyclopædia Britannica, Inc.

After completing this example, you will learn how to set up RedOx reactions in OLI Studio: Stream Analyzer and Corrosion Analyzer.

### Starting the Simulation

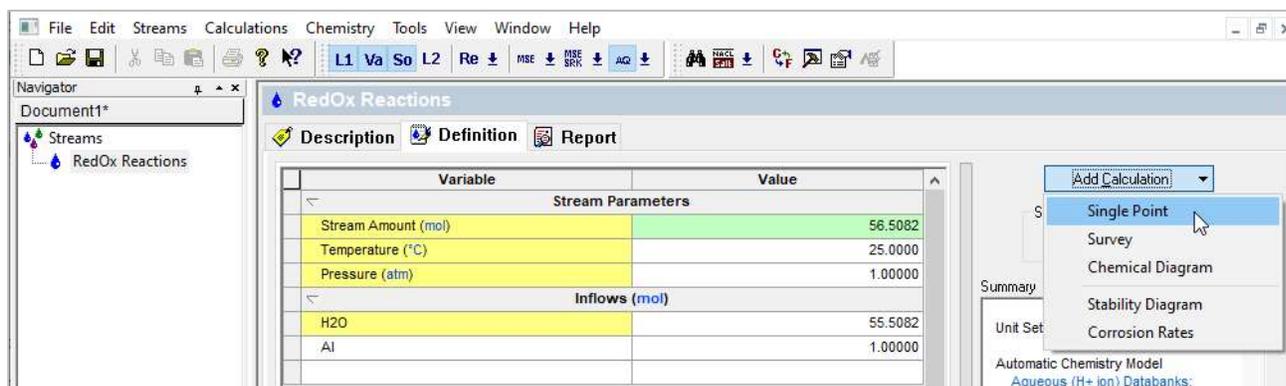
All instructions will be represented by a check mark ✓

- ✓ To start the software, double-click the OLI Studio icon on the desktop , which will take you to the OLI Studio interface where you can start creating your calculations.

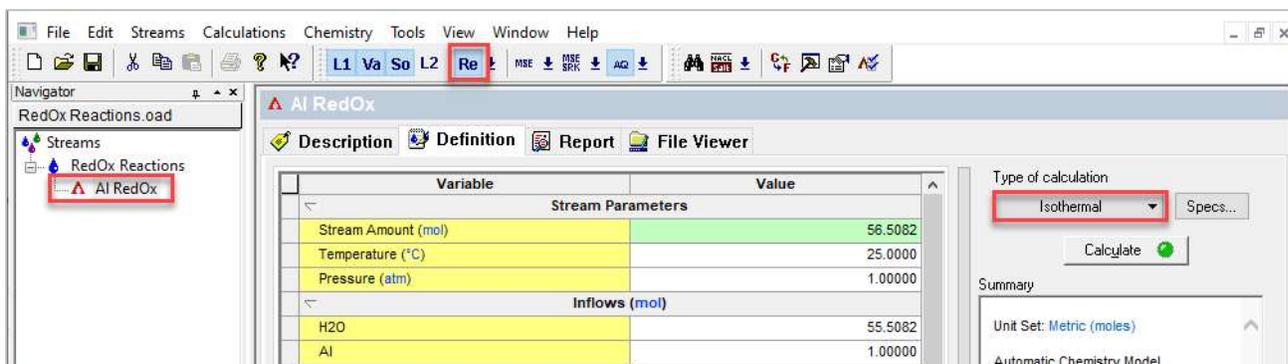
Use the inputs and parameters from the table below to create the stream's composition. Certain inputs, such as the name style, units, etc. will require further adjustments, and will be described as necessary.

Basic RedOx calculation					
Stream Name	RedOx Reactions	Stream Amount	Calculated	Inflows (mol)	
Name Style	Formula	Temperature	25 °C	H2O	55.5082
Framework	AQ	Pressure	1 atm	Al	1
Units sets	Default (mol)				

- ✓ Add a new stream  and rename it **RedOx Reactions**
- ✓ Enter the inflows from the table below
- ✓ Add a **Single Point** calculation



- ✓ Select an **Isothermal** calculation, and change the name of this new calculation as **Al RedOx**
- ✓ Select the **Re** button – it should turn light blue



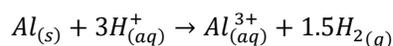
- ✓ Click on the down-arrow next to the **Re** button, you can see that the Aluminum oxidation/reduction reactions have been checked automatically



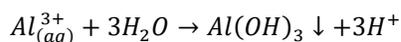
- ✓ Click on the **calculate** button -
- ✓ Click on the **Report** tab and scroll down to the **Element Balance** table

	Total	Aqueous	Vapor	Solid
	mol	mol	mol	mol
H(+1)	108.016	104.919	0.0973386	3.0
Al(+3)	1.0	7.78818e-9	0.0	1.0
O(-2)	55.5082	52.4596	0.0486693	3.0
H(0)	3.0	1.43707e-3	2.99856	0.0
O(0)	2.59617e-83	1.99877e-86	2.59418e-83	0.0

The electrochemical reaction that took place was:



This means that 1 mol of Al was converted to 1 mol of  $Al^{3+}$ , and that 3 moles of molecular hydrogen ( $H^0$ ) were created. However, the  $Al^{3+}$  appears all in the solid phase. This is because  $Al^{3+}$  hydrolyses and causes the formation of  $Al(OH)_3$  precipitate as shown by the reaction below.



## No Transition Metals

In this example, Na<sub>2</sub>S will be added to the stream. This means that we have introduced Sodium and Sulfur ions to the system (no transition metals). And their respective oxidation states are +1 and -2.

- ✓ Add a **single point** calculation and rename it **Na2S**
- ✓ Add 0.1 moles of Na<sub>2</sub>S under **inflows**
- ✓ Select the **Re** button

**Note:** Click on the down-arrow next to the **Re** button, and you can see that the Aluminum is the only element that has been selected to include oxidation/reduction reactions. Sodium and Sulfur are not turned ON by default.

- ✓ Click on the **calculate** button

The screenshot shows the software interface for the 'Al-Na2S' calculation. The 'Re' button is selected, and a dropdown menu is open showing 'Aluminum' selected. The 'Calculate' button is highlighted. The 'Stream Parameters' table is visible, showing 'Stream Amount (mol)' as 56.6082, 'Temperature (°C)' as 25.0000, and 'Pressure (atm)' as 1.00000. The 'Inflows (mol)' table shows 'H2O' as 55.5082, 'Al' as 1.00000, and 'Na2S' as 0.100000.

Variable	Value
<b>Stream Parameters</b>	
Stream Amount (mol)	56.6082
Temperature (°C)	25.0000
Pressure (atm)	1.00000
<b>Inflows (mol)</b>	
H2O	55.5082
Al	1.00000
Na2S	0.100000

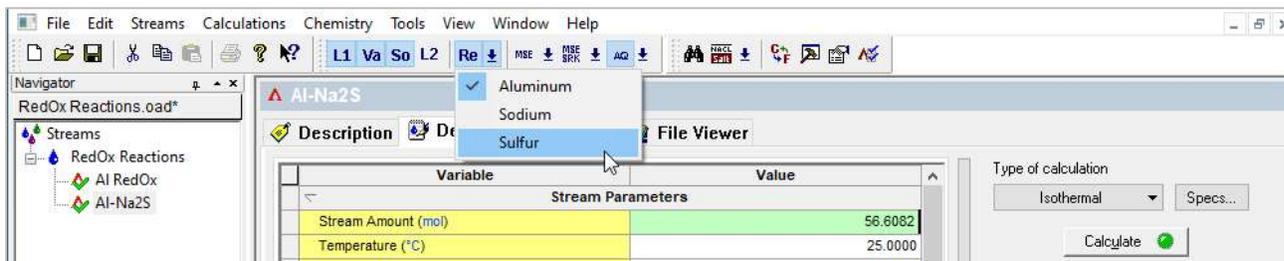
- ✓ Click on the **Report** tab and scroll down to the **Element Balance** table

The screenshot shows the software interface for the 'Al-Na2S' calculation. The 'Report' tab is selected, and the 'Element Balance' table is displayed. The table shows the following data:

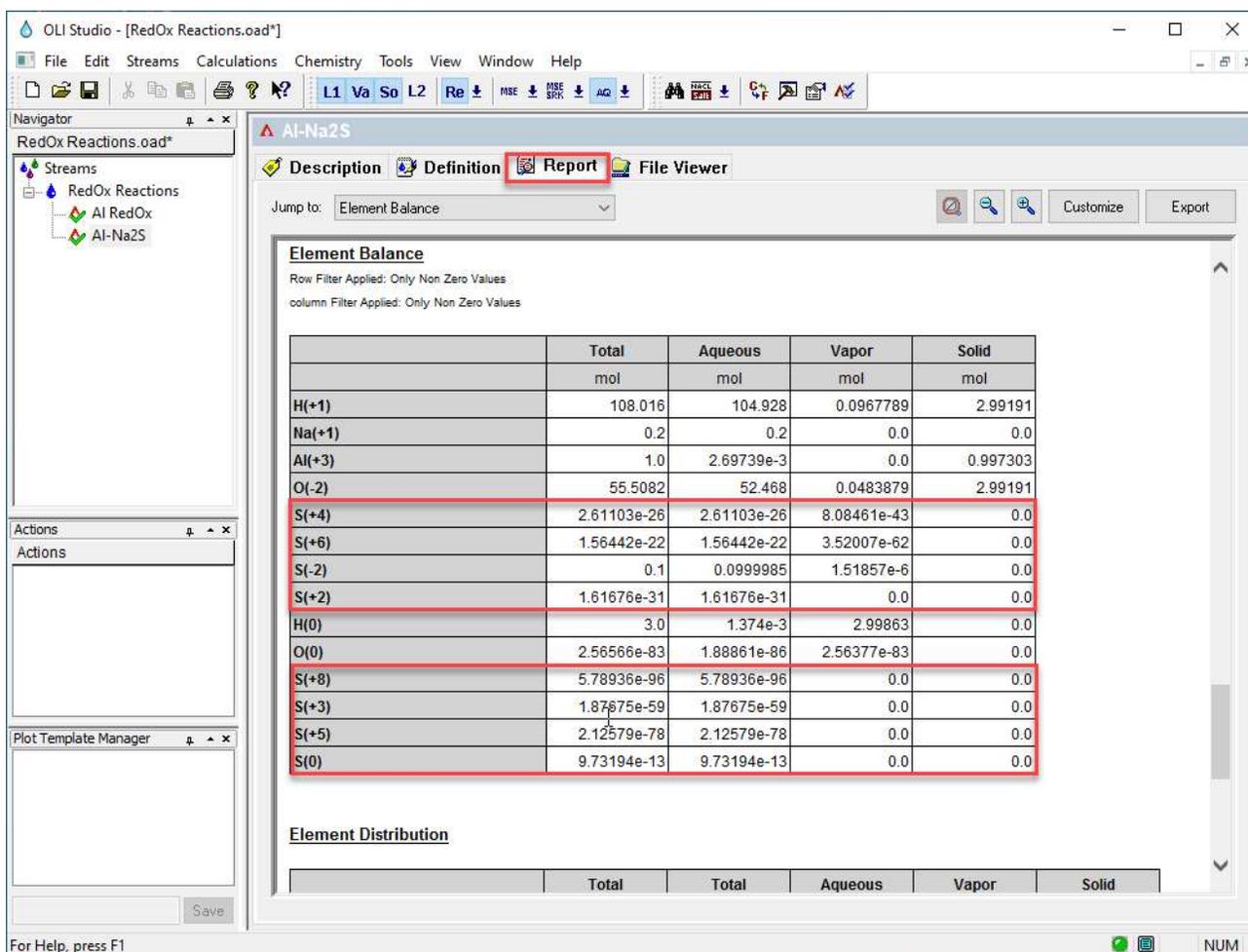
	Total mol	Aqueous mol	Vapor mol	Solid mol
H(+1)	108.016	104.928	0.0967789	2.99191
Na(+1)	0.2	0.2	0.0	0.0
Al(+3)	1.0	2.69739e-3	0.0	0.997303
O(-2)	55.5082	52.468	0.0483879	2.99191
S(-2)	0.1	0.0999985	1.51857e-6	0.0
H(0)	3.0	1.374e-3	2.99863	0.0
O(0)	2.56566e-83	1.88861e-86	2.56377e-83	0.0

Notice that we entered Sulfur a S-2, the software is assuming that the oxidation state for the calculation is the oxidation state that you entered in the inflows, which in this case would be -2. We know that Sulfur can have

several oxidation states, but we did not instruct the software to account for them. If you want to include the oxidation/reduction reactions of Sulfur, you need to turn the ON manually by clicking on it.



- ✓ Enable **Sulfur** redox reaction by clicking on it
- ✓ Click on the **calculate** button
- ✓ Click on the **Report** tab and scroll down to the **Element Balance** table



Notice that 8 different oxidation states for Sulfur have been enabled. The predominant oxidation state under these conditions is S-2. All the other ones are virtually zero.

How do I select only oxidation states that I am interested on?

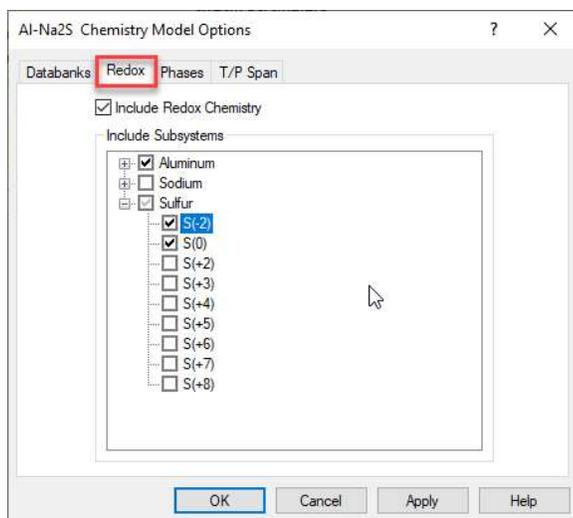
## Selecting Specific Oxidation States

If you want to enable specific oxidation states for Sulfur, the software gives the option to select specific oxidation states.

- ✓ Go back to the definition tab, and then go to **Chemistry > Model Options...**



- ✓ A new window opens. Select the **Redox** tab and expand the **Sulfur** subsystem. In here you can enable and disable all or specific oxidation states. Let's say we want to include the following oxidation states: -2 and 0 only, so the window will look like the image below.
- ✓ Click **OK**



- ✓ Click on the **calculate** button

**Note:** You can double check the selection by clicking on the down-arrow next to the **Re** button, and you can see that the Sulfur now shows the two selected oxidation states.



- ✓ Click on the **Report** tab and scroll down to the **Element Balance** table

The screenshot shows the OLI Studio interface with the 'Report' tab selected. The 'Element Balance' table is displayed, showing the distribution of elements across different phases and oxidation states. The table is filtered to show only non-zero values.

	Total	Aqueous	Vapor	Solid
	mol	mol	mol	mol
H(+1)	108.016	104.928	0.0967789	2.99191
Na(+1)	0.2	0.2	0.0	0.0
Al(+3)	1.0	2.69739e-3	0.0	0.997303
O(-2)	55.5082	52.468	0.0483879	2.99191
S(-2)	0.1	0.0999985	1.51857e-6	0.0
H(0)	3.0	1.374e-3	2.99863	0.0
O(0)	2.56566e-83	1.88861e-86	2.56377e-83	0.0
S(0)	9.7322e-13	9.7322e-13	0.0	0.0

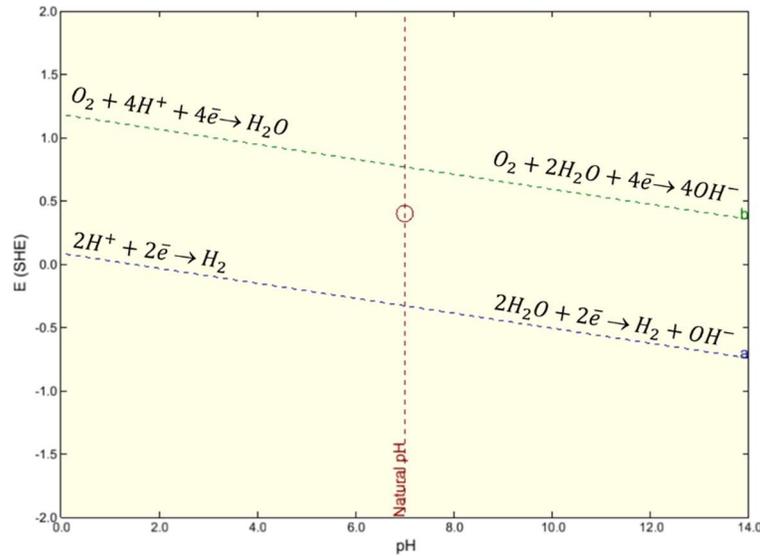
Notice that only the two selected oxidation states are shown in the report table, with S-2 being the most stable oxidation state.



## Water Stability Region, ORP and Natural pH

Water can act as both an oxidant agent, in which case the water is reduced to  $H_2$ , and a reducing agent, in which water is oxidized to  $O_2$ . If a chemical species is to be stable in aqueous solution, it must not react with the water through a redox process. In other words, the oxidation and reduction potentials of the species must be such that it is thermodynamically unfavorable for the species to be either oxidized or reduced by water.

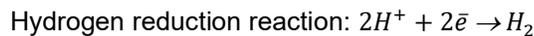
The diagonal dashed lines, represented by the letters **a** and **b** are the water reduction and water oxidation lines, respectively.



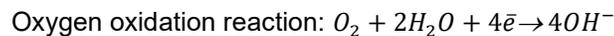
Stability field of water

Below the water reduction line (a): Water decomposes to form  $H_2$  gas. Above the water oxidation line (b): Water decomposes to form  $O_2$  gas. The region within these lines (**a** and **b**) is called the stability region of water.

In an acid solution, the primary redox reactions are:



In a basic solution, the primary redox reactions are:



In acidic solutions, the relevant reduction reaction is the reduction of  $H^+$  to  $H_2$ :



Hence, the potential for the reduction of  $H^+$  to  $H_2$  is:

$$E = 0 - 0.059 \log\left(\frac{1}{[H^+]}\right) = -0.059 \text{ pH (V(SHE))} \quad \text{Equation 2}$$

Assuming H<sub>2</sub> gas is at 1 atm, and V(SHE) is units of volts referenced to the Standard Hydrogen Electrode.

Equation (2) is shown in the above figure as the blue dash line, labeled **a**.

When water acts as the reducing agent, in acidic solutions, the relevant half reaction is:



And the potential (E) is given by:

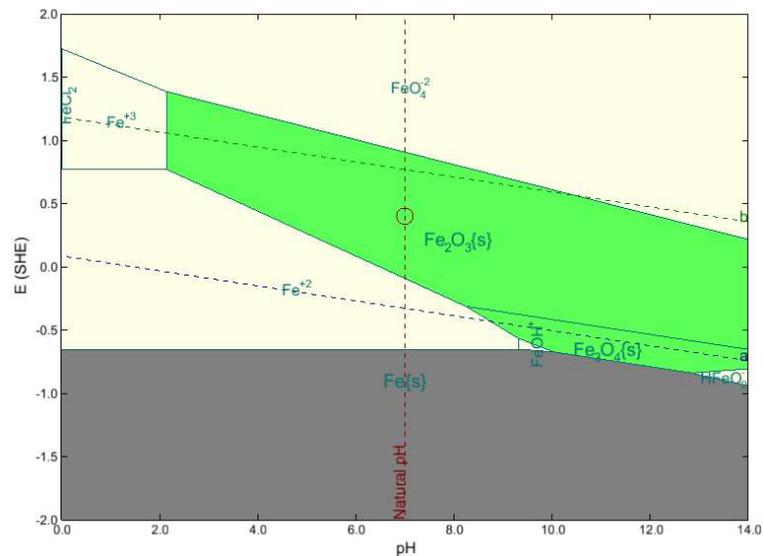
$$E = 1.23 - 0.059 \text{ pH } (V(SHE)) \quad \text{Equation 4}$$

Equation 4 is shown in the above figure as the green dashed line, label **b**. Remember that this is a reduction potential, so for water to be oxidized, the species that is going to be reduced must have a reduction potential that is more positive than 1.23V at pH=0. This requires a fairly strong oxidizing agent.

The values of the **Natural pH** and the **Oxidation Reduction Potential (ORP)** are superimposed on the above diagram. The natural pH line of the water sample is the water's computed pH before it is adjusted using with acid or base to create the diagram. The ORP is represented by the red circle and indicates the initial electrochemical potential of the water phase. This is the value before the potential is adjusted using a potentiostat, for example.

## Passivity Region

The green color represents the range of possible passivation. It is the stability field of a sparingly soluble compound (usually an oxide or hydroxide or salt). This compound will form a layer on the surface of the metal, which may protect the metal from corrosion. Having determined that a layer is formed, it is necessary to verify whether it is protective or not because this depends on the crystalline structure of the sparingly soluble compound.



In the above plot, the green area contains Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> as the solid phases produced by oxidation of Fe. These films dramatically reduce the rate of corrosion through several mechanisms.

One mechanism through which passive film reduce corrosion is to act as a transport barrier. The film reduces the mass-transfer-limited current density of a species that must diffuse from the bulk solution to the metal surface in order to react. Another mechanism is that the film may block reaction sites on the surface preventing further corrosion.

It has been observed that the corrosion rate is reduced substantially by the forming film even where there is not visible evidence of the film yet. This would be the case when only one or two monolayers have formed.

## Immunity Region

The gray color represents the immune to corrosion region. It is the stability field of the elemental metal. Fe is the base metal in the above plot.

## Corrosion Region

The light-yellow color represents the corrosion region. It is the stability field(s) of dissolved (ionic or neutral) metal species in which neither the metal nor passivating solids are stable. In the above plot,  $\text{Fe}^{2+}$  is the ionic species that is the most stable.

## Limitations

Some limitations of stability diagrams include:

- No information on corrosion kinetics is provided by these thermodynamically derived diagrams
- The diagrams are derived for specific temperature and pressure conditions
- In areas where a stability diagrams shows oxides to thermodynamically stable, these oxides are not necessary of a protective (passivating) nature.

## Real Solution Stability Diagrams

The diagrams generated by OLI software are not the same as those that appear in Pourbaix's "Atlas of Electrochemical Equilibria in Aqueous Solutions<sup>1</sup>." Through OLI's electrochemical thermodynamic engine, real activity coefficient for virtually any aqueous chemistry can be generated at any temperature and pressure supported by thermodynamic engine.

The thermodynamic engine will also calculate the required phase separation for the composition and conditions given and use the resulting aqueous phase for the stability diagram generation. This ensures an answer as close as possible to real world observed conditions.

### Building the Fe in Water Pourbaix Diagram

After completing this example, you will learn how to set up a Pourbaix Diagram using the **Stability Diagram** tool.

There are several steps when creating a Pourbaix diagram:

- Environment Creation
- Selecting the right titrants
- Selecting the metallic surface
- Formatting – Optional

#### Environment Creation

The chemical environment in which a particular metal will corrode needs to be entered before the stability analysis can be calculated, even if the environment is just pure water.

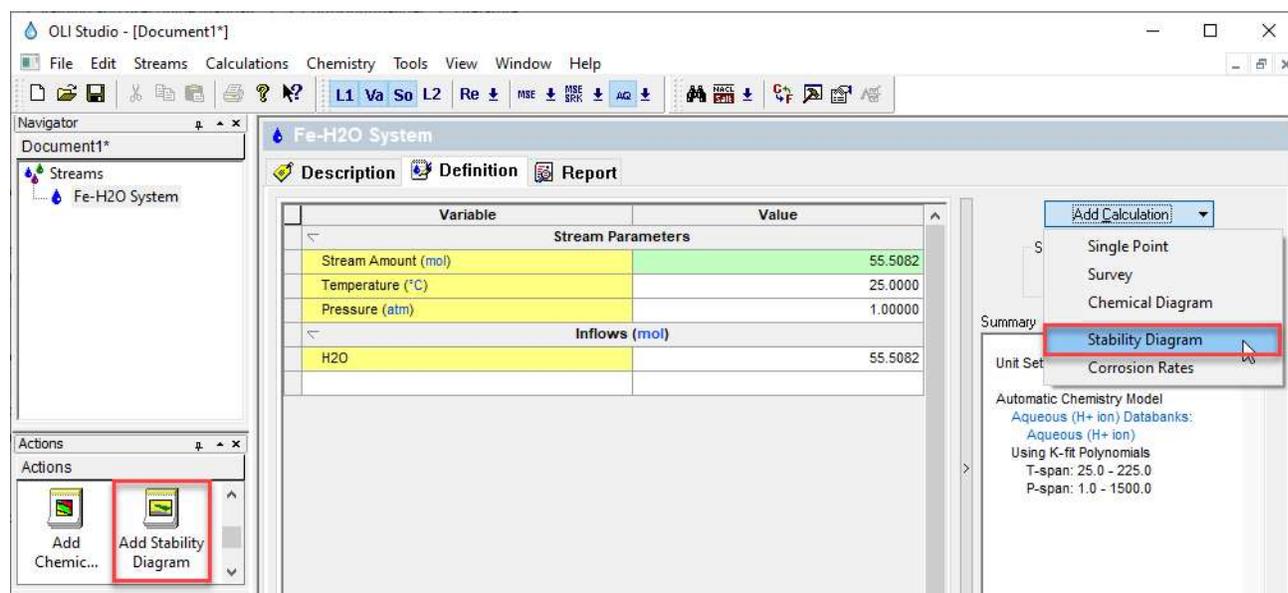
There are two ways of entering the data depending on the form. If all the species are neutral, i.e. NaCl or H<sub>2</sub>S, then the **Add Stream** is sufficient. On the other hand, if the environment includes ionic species concentrations, i.e. Na<sup>+</sup>, Cl<sup>-</sup>, the **Add Water Analysis** option is needed.

For this example, we are going to use the **Add Stream** option. Use the inputs and parameters from the table below to create the stream's composition. Certain inputs, such as the name style, units, etc. will require further adjustments, and will be described as necessary.

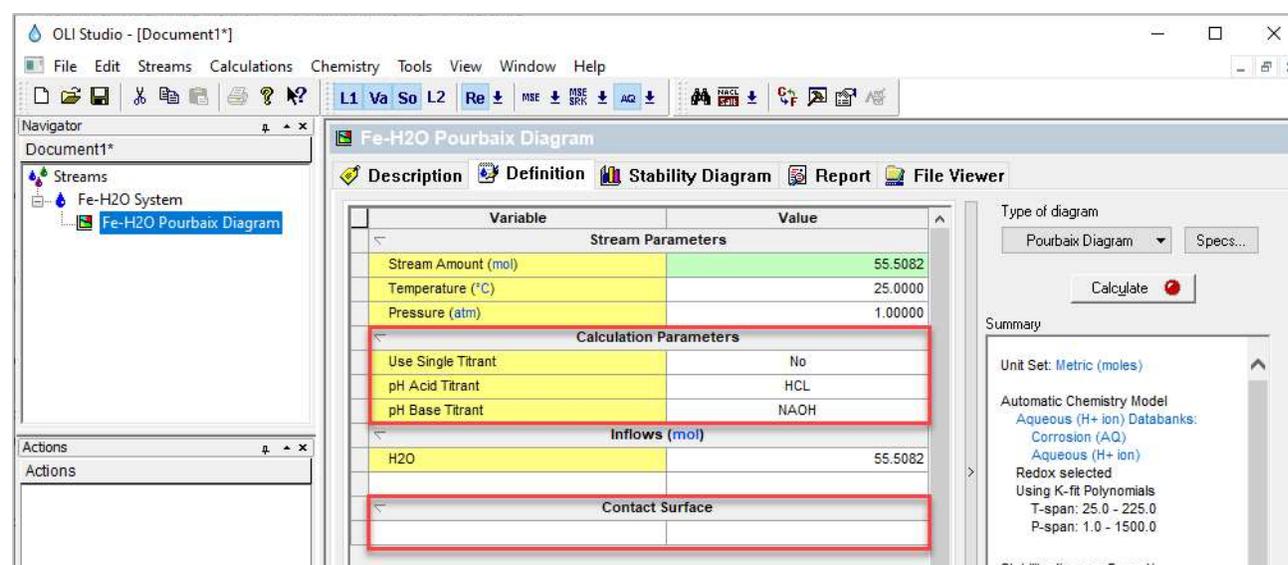
Stability Diagram Calculation			
Calculation Settings		Stream Composition and Conditions	
Stream Name	Fe-H2O System	Stream Amount	55.5082 (Calculated)
Framework	AQ	Temperature	25 °C
Calculation Type	Stability Diagram	Pressure	1 atm
		pH Range	0-14
		H2O	55.5082 moles
		Contact Surface	Fe

<sup>1</sup> Pourbaix, M. 1966. Atlas of electrochemical equilibria in aqueous solutions. Houston, Tex.: National Association of Corrosion Engineers

- ✓ Add a new **Stream**
- ✓ **Click** on the new Stream and press **<F2>** to change the name to *Fe-H2O System*
- ✓ Leave **H2O** as 55.5082 moles
- ✓ Leave the default temperature and pressure
- ✓ Go to the **Add Calculation** button and select **Stability Diagram** calculation or by selecting the **Stability Diagram** icon in the Actions Pane.



- ✓ Select **Pourbaix Diagram** as Type of Survey – Default
- ✓ **Click** on the new icon *Stability Diagram* and press **<F2>** to change the name to *Fe-H2O Pourbaix Diagram*



**Note:** Notice that two new sections appear in the **Definition** tab: **Calculation Parameters** and **Contact Surface** grids. Additionally, the Redox button **Re** is turned ON.

In the **Calculation Parameters** grid is where the pH titrants need to be defined. These default pH titrants selected by default are HCl and NaOH. You have the option to change the default titrants to your preferred titrants.

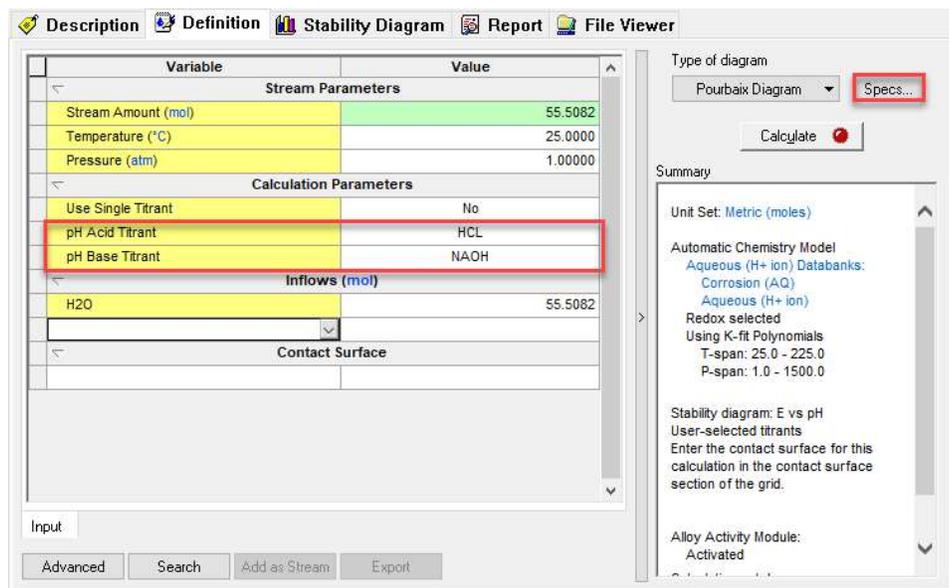
In the **Contact Surface** grid is where the metal or alloy of interest needs to be defined. E.g. Fe, Cu, carbon steel, etc.

The **Redox** button (Re) is turned ON for this calculation since reduction and oxidation reactions are needed to create the Pourbaix Diagram. This option will enable the different oxidation states of the selected metal.

## Selecting the right titrants

Since the real chemistry is used to generate the diagrams, real chemistry must be used to move the pH away from the natural pH of the specified chemistry to sweep through the desired range of pH. Therefore, an acid titrant and a base titrant must be specified. By default, the software used HCl and NaOH titrants, as shown in the figure below. One will always have the  $H^+$  and  $OH^-$  ions present with the water. HCl is chosen as the acid because chloride ions generally do not form complexes with many species until the system is strongly acidic. NaOH is used because it is the complementary base from the NaCl salt.

The titrants can be changed by going to the **specs...** button. A dialog box will be displayed on which you need to select the **Axes** category and then the **pH Titrant** option.



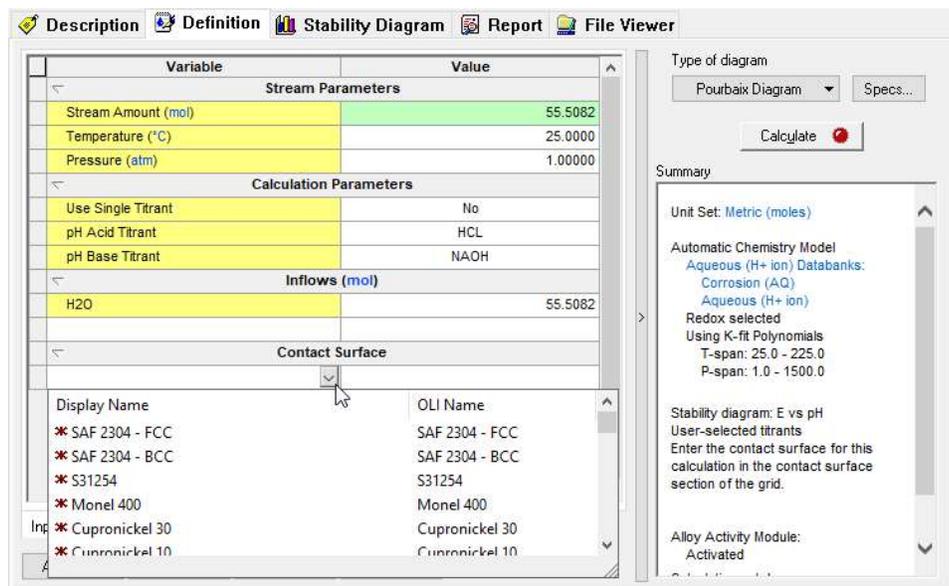
Default titrants HCl and NaOH are added to the defined chemistry to move along the x-axis of the stability diagram. The default titrants can be changed by clicking on the Specs... button.

- ✓ Leave the default titrants for this calculation: HCl and NaOH

## Selecting the Contact Surface

The only requirement before the calculate button can be clicked, is to select the '**Contact Surface**' that will be studied.

The 'Contact Surface' is the metallic material for which the stability is to be studied. It can be selected by using the drop-down list as shown in the image below. All the possible contact surfaces will be listed in the drop list.



If an alloy (always the top several surfaces listed) is selected, only one contact surface can be selected. If pure components, i.e., Fe, Cr, Mo, are selected, several contact surfaces can be selected and will listed in series as shown below.

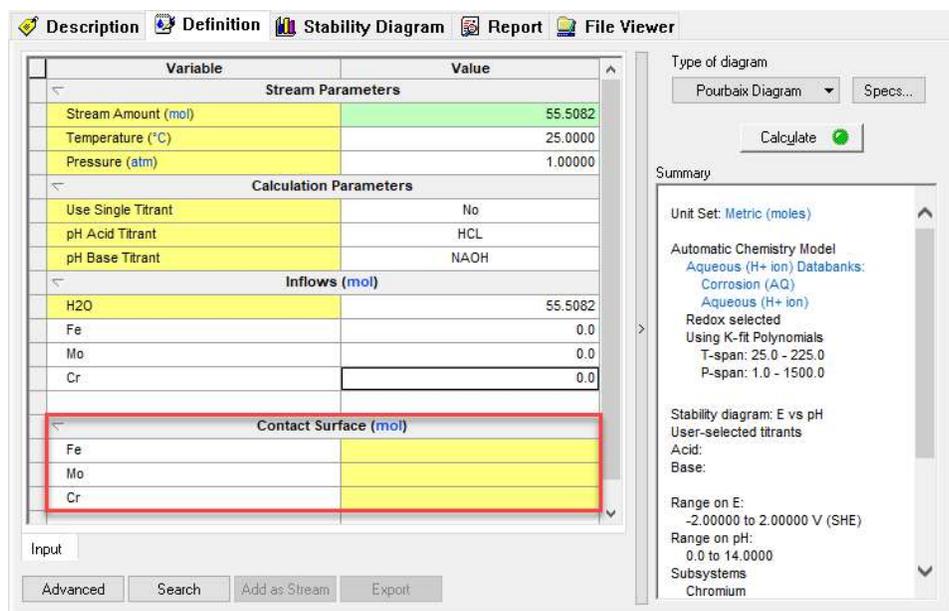


Figure 1. Several pure components (elements) can be selected or only one alloy can be selected.

- ✓ Under the **Contact Surface** grid type **Fe**
- ✓ Click on the **Calculate** button <F9>

OLI Studio - [Document1\*]

File Edit Streams Calculations Chemistry Tools View Window Help

Fe-H2O Pourbaix Diagram

Variable	Value
<b>Stream Parameters</b>	
Stream Amount (mol)	55.5082
Temperature (°C)	25.0000
Pressure (atm)	1.00000
<b>Calculation Parameters</b>	
Use Single Titrant	No
pH Acid Titrant	HCL
pH Base Titrant	NAOH
<b>Inflows (mol)</b>	
H2O	55.5082
Fe	0.0
Mo	0.0
Cr	0.0
<b>Contact Surface (mol)</b>	
Fe	

Summary

Unit Set: Metric (moles)

Automatic Chemistry Model

- Aqueous (H+ ion) Databanks:
  - Corrosion (A.Q)
  - Aqueous (H+ ion)
- Redox selected
- Using K-fit Polynomials
- T-span: 25.0 - 225.0
- P-span: 1.0 - 1500.0

Stability diagram: E vs pH

User-selected titrants

Acid:

Base:

Range on E: -2.00000 to 2.00000 V (SHE)

Range on pH: 0.0 to 14.0000

Subsystems

Iron

For Help, press F1

At this point all the basic inputs to create a Pourbaix Diagram have been defined. However, you can change these default values if you prefer.

## Diagram Ranges

Notice that in the summary box (see above plot) the following default plotting settings have been defined: Potential range: -2 to 2 V vs SHE and pH range: 0-14.

You can change these defaults in the **Definition** tab, by clicking on the **Specs...** button and then selecting **Axes**. This opens a new window.

OLI Studio - [Document1\*]

File Edit Streams Calculations Chemistry Tools View Window Help

Fe-H2O Pourbaix Diagram

Definition

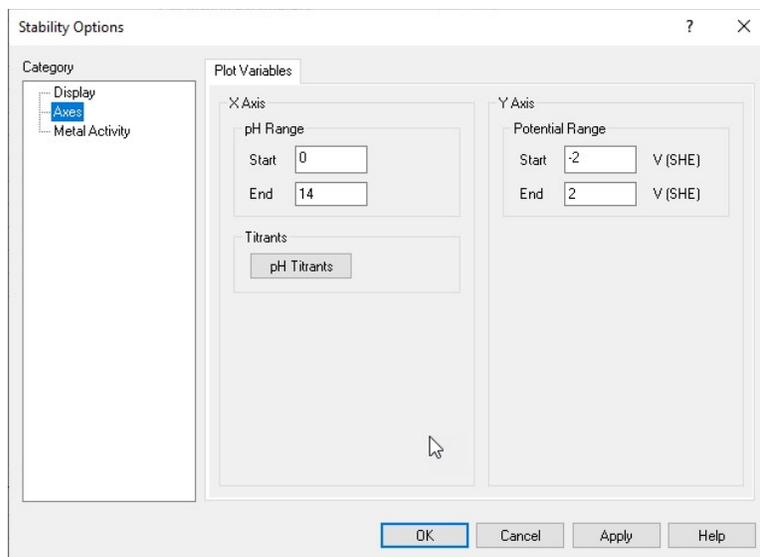
Variable	Value
<b>Stream Parameters</b>	
Stream Amount (mol)	55.5082
Temperature (°C)	25.0000
Pressure (atm)	1.00000

Type of diagram

Pourbaix Diagram

Specs...

Calculate



## Trace Species (Metal Activity)

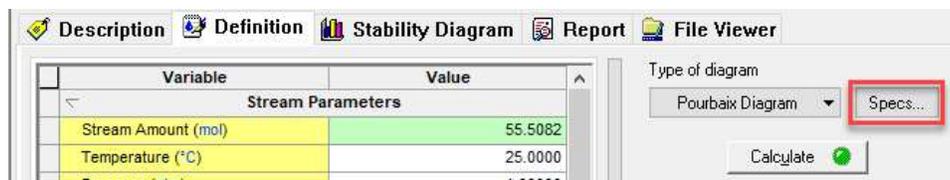
If the bulk chemistry does not contain any amount of the species used as the contact surface, an activity ( $a_i = m_i \gamma_i$ ) must be assumed in order to find the predominant solids. In the work done by Pourbaix, and activity of  $10^{-6}$  was used. For instance, is a contact surface of iron was used, but iron was not part of the bulk chemistry, there would be a singularity in the Nernst Equation for the oxidation of iron, i.e.

$$e = e^o - \frac{RT}{2F} \ln \frac{a_{Fe}}{m_{Fe^{2+}} \gamma_{Fe^{2+}}} \quad \text{Equation 5}$$

Where  $m_{Fe^{2+}} \gamma_{Fe^{2+}}$  would be equal to zero.

By decreasing the assumed value, the areas of stability for solid films will decrease. This may be useful for simulating systems with high fluid velocities.

You can change the trace default value in the **Definition** tab, by clicking on the **Specs...** button and then select **Metal Activity**.



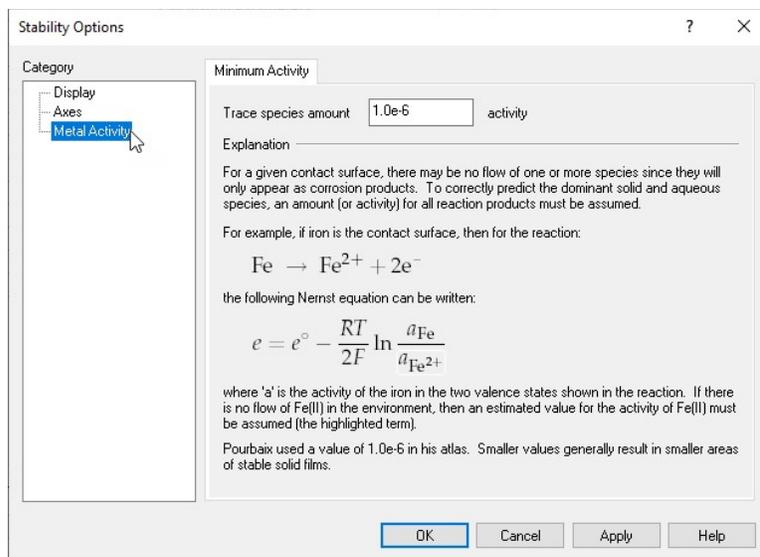
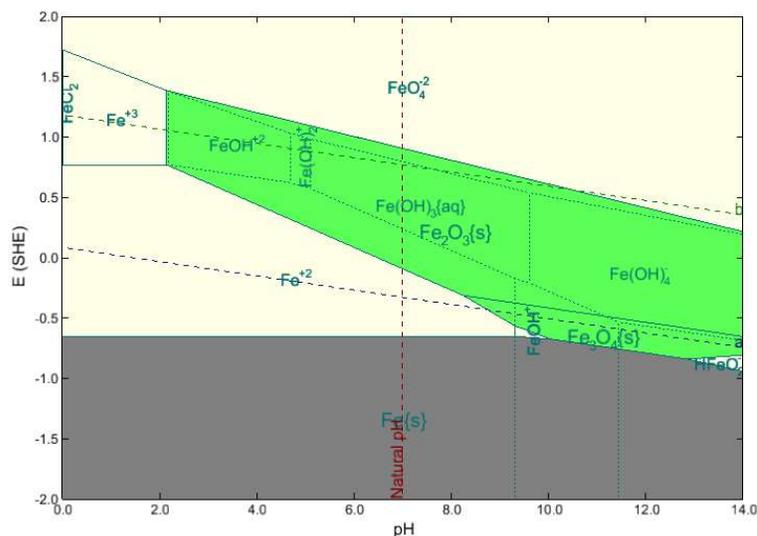


Figure 2. Setting the minimum activity for trace species

The default value for the Metal Activity is 1e-6.

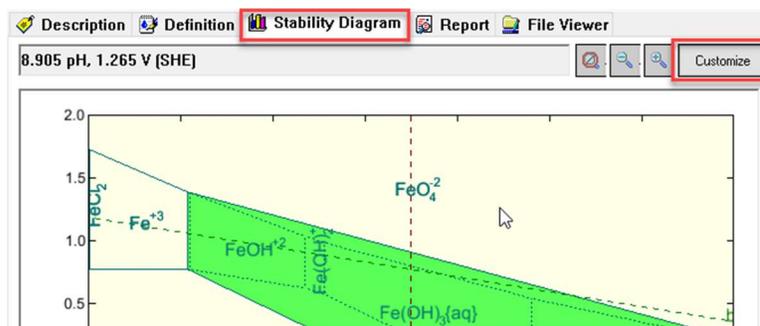
✓ To check the results, click on the **Stability Diagram** tab. You will see a diagram similar to the one below



## Diagram Editing

The results shown in the diagram are organized in oxidation/reduction subsystems. A redox subsystem consists of a base species in its neutral state, say Fe, and all of its possible oxidation states, which for Fe would be Fe, Fe<sup>+2</sup>, Fe<sup>+3</sup>, and FeO<sup>+2</sup>. Each system contains the set of predominant solids and aqueous species that can be formed from the bulk chemistry and the given metal system. When more than one metal is given in the contact surface, one must look at all of the redox subsystems to get an idea of what stable films may form and at what conditions they will form.

The edit how to display each oxidation/reduction system you can click on the **“Customize”** button.

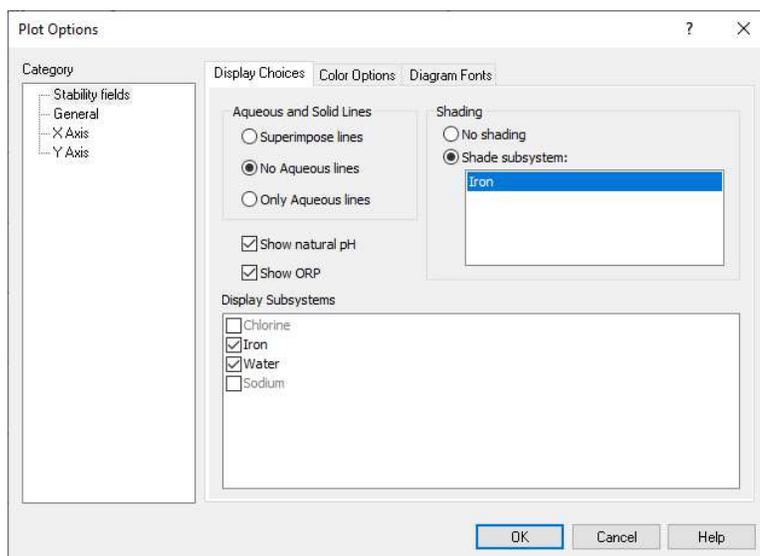


This opens a new window. Under the **Display Choices** tab, you can find the following sections:

1. **Aqueous and Solids Lines:** The dominant aqueous species in equilibrium with the solids can be turned off by selecting “**No aqueous lines**”. The dominant aqueous species in the regions where there are no solids are still displayed.  
 Selecting “**Only aqueous lines**” will show both the aqueous species in equilibrium with solids and the aqueous species where there are no solids, but no solids will be displayed.  
 Selecting “**Superimpose lines**” will show both aqueous and solids lines.
2. **Show Natural pH:** The Corrosion Analyzer uses your real process fluid definition and conditions to calculate the natural phase separation. It also accurately predicts the pH of the bulk aqueous fluid. The pH at the specified conditions of the problem definition is represented by a vertical line labeled “Natural pH”.
3. **Show ORP:** The software will place a circle that represents the oxidation reduction potential of the bulk solution.
4. **Display Subsystems:** Here you can overlay subsystems. To overlay subsystems, simply check the desired subsystem. The water subsystems show both the ‘a’ and ‘b’ line. Grayed subsystems cannot be included until the redox option for this system is turned on in the chemistry.
5. **Shading:** Only one of the selected redox sub-systems can be shaded. All others are drawn as lines.

- ✓ Click on the **Customize** button, and make the following selections:
  - No Aqueous Lines
  - Show ORP

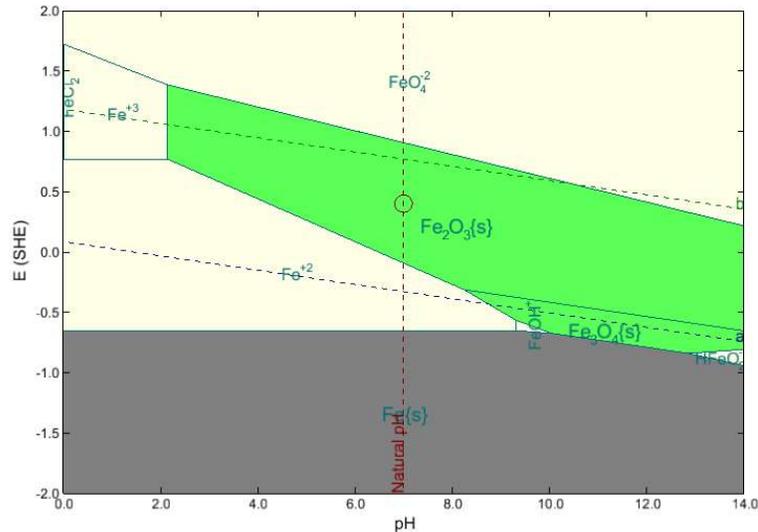
- ✓ Click **OK**



It is time to **save** your file (**File >Save as...**) or using the **save** icon in the tool bar. You can save it and name it as *Stability Diagrams*.

## Analyzing the Results

The Pourbaix Diagram for the Fe-H<sub>2</sub>O system at 25 °C and 1 atm should look like the image below:



The obtained diagram is useful for assessing the corrosion behavior of iron in pure water.

Elemental iron (gray section) is stable from -2 to -0.6 V SHE. At a potential greater than -0.6 V SHE, Fe oxidizes to Fe<sup>+2</sup>. If the pH is above 10, the boundary is at a lower potential for example, -0.7 V SHE at 12 pH.

The software computes that Fe<sub>3</sub>O<sub>4</sub> (magnetite) is stable between a pH range of ~8.3 and 12. This is also known as the *Passive Film* that protects the iron surface from active corrosion. At higher potentials, the software computes Fe<sub>2</sub>O<sub>3</sub> (hematite). Hematite is the dehydrated form of Fe(OH)<sub>3</sub> and FeOOH, two forms of rust. These phases provide less corrosion protection the iron surface than the magnetite. These two phases are represented in the plot by the green color.

The light-yellow sections of the plot represent the dominant iron-containing species dissolved in solution. The species with the largest range is Fe<sup>+2</sup>. The software computes stability for this species from -0.6 V to 0.77 V SHE, at low pH, and it is no longer stable at pH 10. Active corrosion of the iron surface is predicted if the pH is between 0 and 10. The actual corrosion rate cannot be predicted from this plot, nor can the pH of the water film (diffusion layer) in contact with the iron surface. Therefore, the pH range of 0 to 10 is a guideline and not a direct prediction.

The natural pH and the oxidation reduction potential (ORP) of water, which is represented by the red circle, are showing that when placing Fe in pure water at 25 °C and 1 atm. The point at which the natural pH and the ORP intersects (7 pH, 0.4 V SHE) indicates that Fe<sub>2</sub>O<sub>3</sub> (hematite) is the most stable species that forms.

Additionally, notice that the oxidation of iron can be coupled with the reduction of water because water reduction line (line **a**) lies above the lines that represent the oxidation of iron. Therefore, corrosion of iron can occur with the evolution of hydrogen and formation of soluble iron-containing ions e.g. Fe<sup>2+</sup>.

## Modeling the Effects of Hydrogen Sulfide on Corrosion

The H<sub>2</sub>S (S<sup>-2</sup>) forms a relatively insoluble precipitate with Fe<sup>+2</sup>. This precipitate has the potential to cover the metal surface and enhance the pH region where iron is protected from the water. We will model this using the Stability Diagram tool.

Use the inputs and parameters from the table below to create the stream's composition. Certain inputs, such as the name style, units, etc. will require further adjustments, and will be described as necessary.

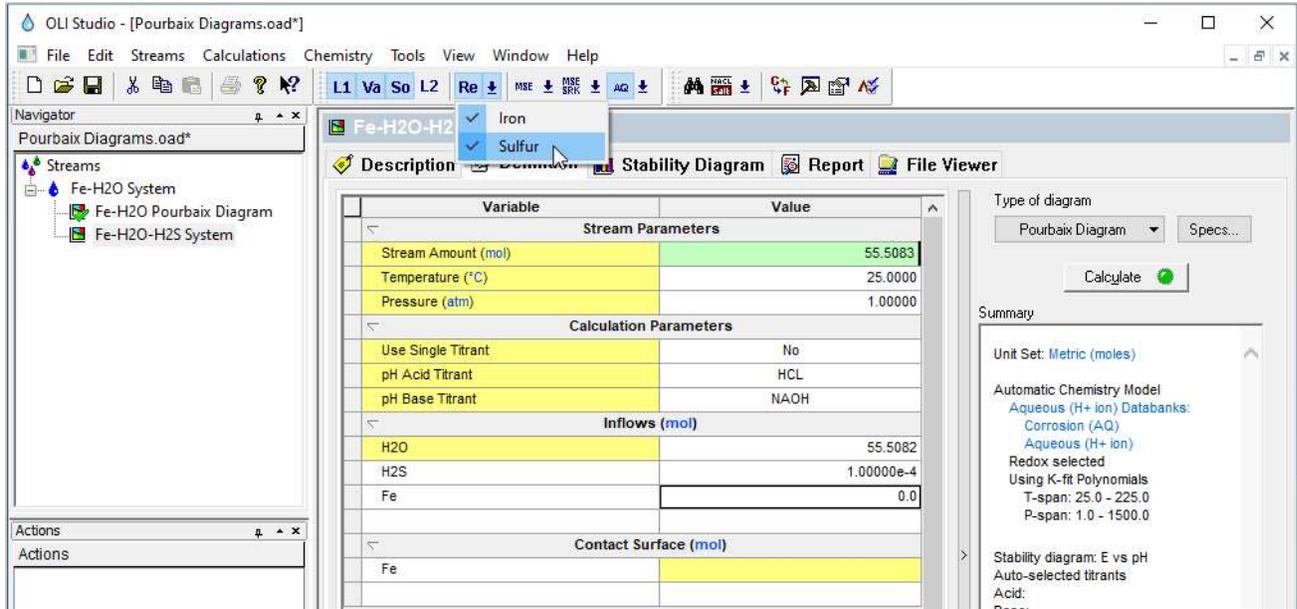
Stability Diagram Calculation			
Calculation Settings		Stream Composition and Conditions	
Stream Name	Fe-H2O System	Stream Amount	Calculated
Name Style	Display Formula	Temperature	25 °C
Unit Set	Metric, Batch, Moles	Pressure	1 atm
Framework	AQ	pH Range	0-14 (Default)
Calculation Type	Stability Diagram	H2O	55.5082 moles
Contact Surface	Fe	H2S	1e-4 moles

- ✓ Under the *Fe-H2O System* add a new Stability Diagram calculation. Go to the **Add Calculation** button and select **Stability Diagram** calculation or by selecting the **Stability Diagram** icon in the Actions Pane.
- ✓ Select **Pourbaix Diagram** as Type of Survey – Default
- ✓ **Click** on the new *Stability Diagram* and press **<F2>** to change the name to *Fe-H2O-H2S System*
- ✓ Enter the composition, temperature and pressure of the stream given in the table above. **Add 1e-4 moles of H2S** as an inflow.
- ✓ Under the **Contact Surface** grid type **Fe**

The screen should look like the image below after all the inputs and definitions have been entered:

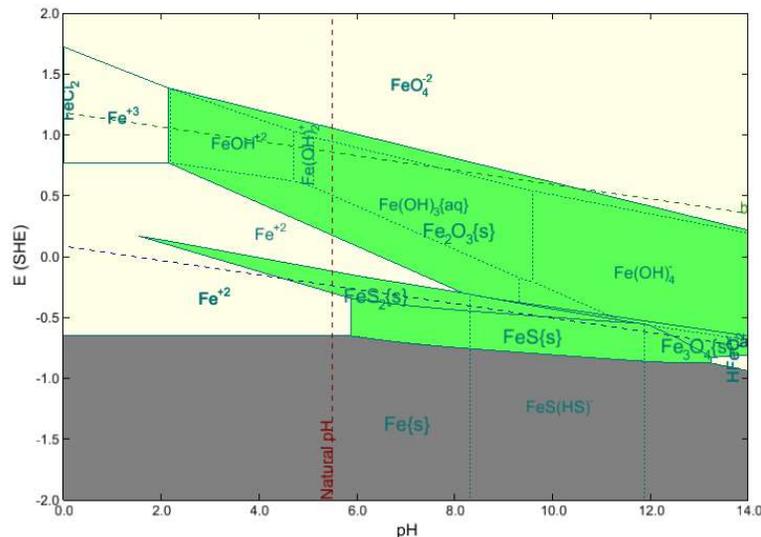
**Note:** By default, only the transition metals are turned ON. The different oxidation states of elements that are not transition metals are not turned on automatically. You need to turn them ON manually. Just as it was discussed in the RedOx section above. You can also select specific oxidation states for Sulfur in **Chemistry > Model Options > Redox**.

- ✓ Go to the **Redox** button (**Re**), and **click** on the drop-down arrow
- ✓ **Select Sulfur**. This will turn the oxidation states of sulfur ON



- ✓ We are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key
- ✓ It is time to **save** your file (**File > Save as...**) or using the **save** icon in the tool bar. You can save it under the same file created in the previous example named *Stability Diagrams*.

## Analyzing the Results



Click on the **Chemical Diagram** tab (  **Stability Diagram** ). This tab displays the Pourbaix Diagram for the Fe-H<sub>2</sub>O-H<sub>2</sub>S system at 25 °C and 1 atm.

Inspection of the diagram reveals a profound effect of H<sub>2</sub>S on the corrosion of iron. New stability fields of FeS and FeS<sub>2</sub> are observed. Elemental iron is found to be in equilibrium with FeS over for pH values ranging from ca. 6.0 to 12.5.

Since the Fe/FeS equilibrium line lies below the H<sup>+</sup> reduction line (**a**), a process consisting of the reduction of H<sup>+</sup> to H<sup>0</sup> and oxidation of Fe to FeS is likely to occur in de-aerated environments. FeS forms a passive film and offers some protection against corrosion.

In fact, the protection due to the formation of FeS is possible over a much wider pH range than that due to the formation of Fe<sub>3</sub>O<sub>4</sub> (magnetite) in the absence of H<sub>2</sub>S. This has important implications for corrosion in refinery installations, where H<sub>2</sub>S is frequently present.

## Chapter III – Corrosion Rates and Polarization Curves

In this chapter we are going to introduce the theory behind the corrosion rate calculations and polarization curves calculated by the software. Then we will jump to hands on exercises.

First, let's start with some corrosion/electrochemistry definitions to understand how corrosion rates and polarization curves are calculated in the software.

### Polarization

Polarization may be defined the shift in electrode potential which results from the effects of current flow with respect to the zero current flow potential. Potential is a thermodynamic variable that can be measured against a suitable reference electrode and has units of volts.

Polarization,  $\eta$ , is the potential change,  $V - E$ , from the equilibrium half-cell electrode potential,  $E$ . Anodic polarization results in  $\eta$  being positive, and cathodic polarization results in  $\eta$  being negative. Both  $V$  and  $E$  are also potentials.

The potentials are measured at the metal/fluid interface. Since metals are very conductive, the measurement point on the metal side can be some distance away without needing a correction, so a wire lead is simply attached to the metal. A reference electrode is used to measure potential in the electrolyte. It must be placed at some distance away from the metal to avoid errors due to transport gradients. However, an aqueous electrolyte has a finite conductivity so there will be an IR drop between the location of the measurement device and the metal surface.

### Reference Electrodes

All voltages in electrolytes are measured with respect to a known chemical reaction, the hydrogen reaction, and the standard hydrogen electrode is used. In practice, the hydrogen electrode is not always useful. Other reference electrodes can be used if they can be limited to a single reversible reaction. When selecting a reference electrode, it must at least have a common ion with one in the electrolyte, and its concentration should not be vanishingly small.

A common reference electrode is the Cu/CuSO<sub>4</sub> which is often used to measure potentials in soil environments such as storage tank bottoms or buried pipelines. A value of 0.337V must be added to a reading from a Cu/CuSO<sub>4</sub> to get the equivalent reading to hydrogen electrode.

In sea water, the Ag/AgCl electrode is often used. It is picked because of the common ion, Cl<sup>-</sup>.

### Reaction Rates

To predict corrosion rate is to predict the rate at which a number of oxidation/reduction reactions will proceed including the metal dissolution reaction. An oxidation/reduction reaction will either consume or produce electrons and must be coupled to another reaction such that the net production of electrons is equal to zero.

### Tafel behavior

The rate at which an electrochemical reaction takes place can often be represented by the Butler-Volmer equation:

$$i = i_o \left[ \exp\left(\frac{\alpha_a F}{RT} \eta_s\right) - \exp\left(-\frac{\alpha_c F}{RT} \eta_s\right) \right] \quad \text{Equation 6}$$

Where  $i_o$  is the exchange current density,  $F$  is the Faraday's constant (96485 equiv/Coulomb),  $\alpha_a$  and  $\alpha_c$  are kinetic parameters,  $R$  is the gas constant and  $T$  is the temperature.  $i_o$  is a function of concentration at the electrode (corroding material) surface and has parameters that must be fit using experimental data. It can be shown that Butler-Volmer type equations can be derived from many simple reactions involving single electron transfers described by Arrhenius type equations. Empirically, it has been shown that the above equation or one of its modifications from the following section, describe nearly all reactions associated with corrosion. Reactions that follow equation 6 are often said to have Tafel kinetics.

## Mass-Transfer Limitations

The reactant  $O_2$  in the equation below



must come from the bulk fluid. It is therefore subject to mass-transfer limitations since it cannot react until it is at the metal/fluid interface. For a given fluid velocity and concentration of  $O_2$ , a maximum rate of transport of  $O_2$  can be calculated from solving the convective diffusion equation:

$$\frac{\partial C_A}{\partial t} + (v^* \cdot \nabla C_A) = D_{AB} \nabla^2 C_A \quad \text{Equation 8}$$

where  $C_A$  refers to the concentration of  $O_2$  and  $D_{AB}$  is the diffusivity of  $O_2$  in water, subject to the boundary conditions

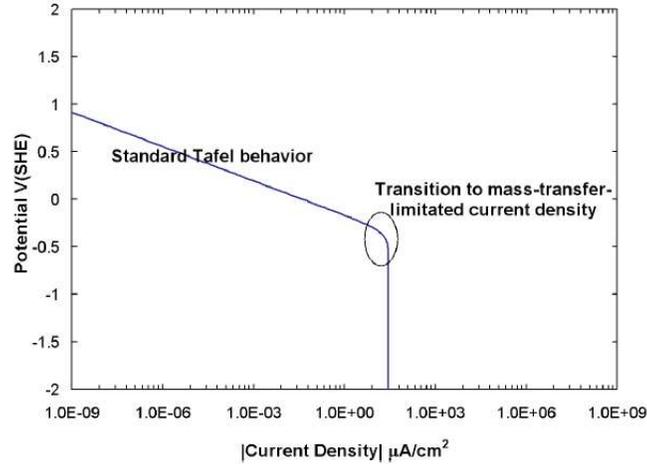
$$C_A = \begin{cases} 0, & \text{at } z = 0; \\ C_\infty & \text{at } z = \delta \end{cases} \quad \text{Equation 9}$$

where  $\delta$  is the length where complete mixing occurs, usually just outside the turbulent boundary layer point. The calculated maximum mass-transfer rate can be converted to a current density,  $i_{lim.O_2}$ , with Faraday's constant. Then, equation 6 can be rewritten as:

$$i_{O_2} = i_o \left[ \exp\left(\frac{\alpha_a F}{RT} \eta_s\right) - \frac{1}{\frac{i_o}{i_{lim.O_2}} + \exp\left(\frac{\alpha_c F}{RT} \eta_s\right)} \right] \quad \text{Equation 10}$$

where the term corresponding to the consumption of  $O_2$  is limited to no more than  $i_{lim.O_2}$ .

The figure below, illustrates how a reaction that has a mass-transfer limitation behaves as the rate goes from activation control (Tafel kinetics) to mass-transfer limitation.



Reaction exhibiting mass-transfer-limited behavior

## Homogeneous Reaction Limitations

$\text{H}_2\text{CO}_3$  can react at the metal surface to form  $\text{H}_2$  and  $\text{HCO}_3^-$  and liberating one electron. In this case, the rate at which  $\text{H}_2\text{CO}_3$  can react is not limited by diffusion, but by how fast it can be formed after it is consumed.

## Mixed Potentials

In a corroding surface, several reactions are occurring simultaneously, and the observed potential is that due to how all of the reactions balance the electrons.

## Net Current

Since the software is valid only within the constraints of aqueous systems, the polarization curves will be bounded by water decomposition reactions. At sufficiently positive potential, the oxygen evolution reaction will occur:



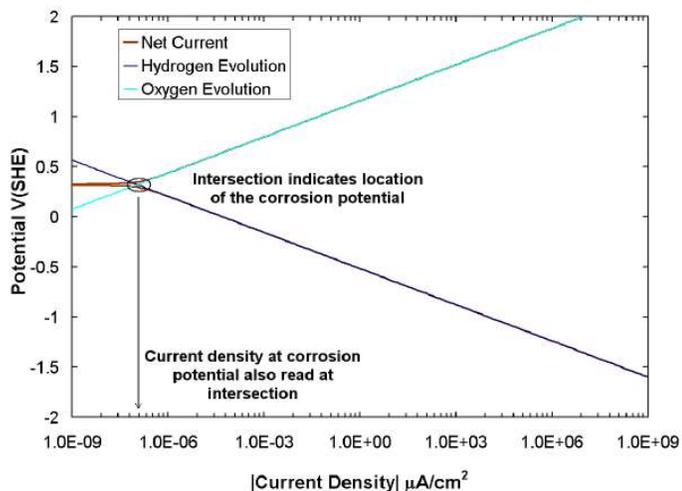
and at sufficiently negative potentials the hydrogen reaction occurs



The rates for the two reactions (10 and 11) can be expressed using equations of the form of (6), or for mass-transfer-limited reactions (7), which are summed to give the net current according to:

$$i_{net} = \sum_j i_{o,j} \left[ \exp\left(\frac{\alpha_{a,j}F}{RT} \eta_{s,j}\right) - \exp\left(-\frac{\alpha_{c,j}F}{RT} \eta_{s,j}\right) \right] + \sum_k i_{o,k} \left[ \exp\left(\frac{\alpha_{a,k}F}{RT} \eta_{s,k}\right) - \frac{1}{\frac{i_{o,k}}{i_{lim,k}} + \exp\left(\frac{\alpha_{c,k}F}{RT} \eta_{s,k}\right)} \right] \quad \text{Equation 13}$$

for  $j$  reactions without mass-transfer limitations, and  $k$  reactions with mass-transfer limitations. The hydrogen and oxygen evolution reactions and the net current are plotted on a log scale as  $E$  vs  $|i|$  in Figure the below, which is also commonly called a *polarization curve*.



Basic polarization curve of water decomposition.

## Open Circuit Potential

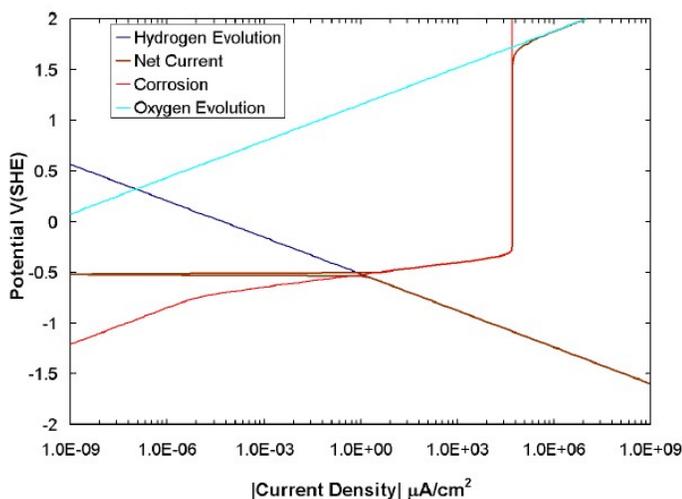
In the figure above, notice that at a potential of 0.322V, the net current approaches a value of zero. The zero point indicates the open circuit potential, or corrosion potential, but the rates of the reactions are not necessarily zero. This is the point where the sum of the rates of all of the reactions at the metal/fluid interface is equal to zero. This point is easily determined experimentally.

## Adding Reactions

If iron was placed in the water, a third reaction becomes possible, i.e. the dissolution of iron:



Adding a line for reaction (13) and adjusting the net current, equation (12), to include the new reaction, produced the plot in Figure 13.



Basic polarization curve with water decomposition and (Fe) corrosion reaction

The open circuit potential has been shifted increasing the rate of hydrogen evolution and decreasing the rate of oxygen evolution. The value of the current density at the new open circuit potential should not be confused with the exchange current density,  $i_0$ , the simultaneous forward and backward rate of a single reaction at steady state. Exchange current is the rate of either oxidation or reduction at the equilibrium electrode. It is expressed as a current. It is also technically a misnomer, since there is no net current flowing.

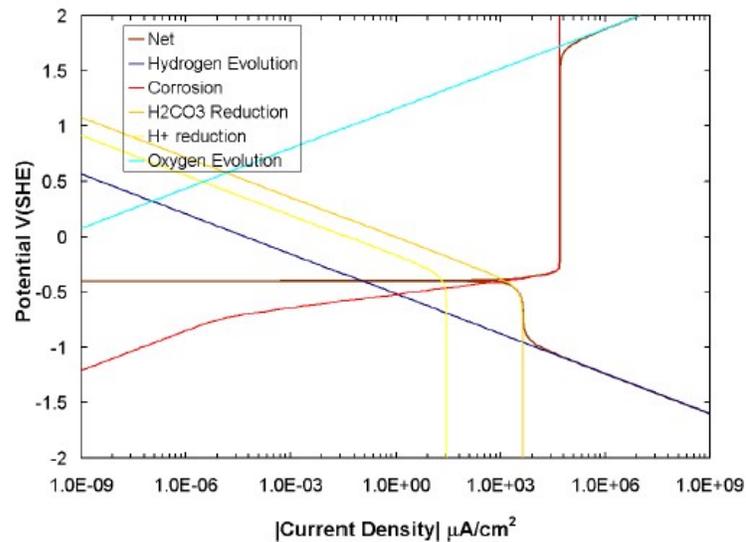
It should be noted that the flattening of the rate of the dissolution of Fe (vertical line) is not necessarily a mass-transfer effect but does reflect the fact that the metal passivates.

Adding  $H_2CO_3$  to the fluid in contact with the metal adds 2 more reactions



Both of these reactions will have mass transfer effect limitations.

The below figure shows the addition of reactions (15) and (16) to the model. The addition pushes up the rate of corrosion and moves the corrosion potential towards a more anodic value. As more components are added, more reactions influencing corrosion may be added to the mixed potential expression. For instance, Figure 5, shows the addition of  $H_2S$  to the system at conditions of saturation and higher temperature. Also note that the changes in conditions affect the corrosion (anodic) polarization shape.



Polarization curve with water decomposition, corrosion reaction and two mass-transfer-limited reactions

Not all corrosion processes proceed by simultaneous reactions on the same surface. When two dissimilar metals are in electrical contact with each other, an electrochemical cell can be established through the process fluid. Then one surface acts as an anode, where the metal corrodes at a higher rate, supplying electrons to the other metal which will now corrode at a lower rate. The reactions on both surfaces remain the same, but at a steady state, neither metal is at its corrosion potential. Sometimes, this effect is purposely used to protect a metal. For instance, zinc and aluminum are used as sacrificial anodes to protect iron or steel hull of ships.

## Net current curve

Of all the curves plotted by OLI Studio: Corrosion Analyzer, only the 'net current' is experimentally measurable. However, many of the underlying reactions can be seen in the curve. At either end are the water decomposition reactions and sometimes a transition to the passive state for the anodic reaction may be observed. When mass-transfer limitations are reached for different reaction, they may be seen as small 'plateaus' in the curve.

## Mass-Transfer Limitations

Figure 15 has a region of the curve circled where a mass-transferred limitation in one reaction influences the next current density. These regions are often called a *plateau* because on a log scale, there is very visible change in current density within a relatively large region of potential. One must change potential sufficiently so that another reaction rate can 'catch up' to the reaction that is mass-transfer-limited.

## Active-to-Passive Transition

In the figure below, the point labeled  $E_{pp}$  denotes the location of the active-to-passive transition. It is the point where increasing potential no longer results in increasing corrosion density. It is caused by the formation of passivating films on the metal surface that either blocks reaction sites by tightly bonding to the metal, or by retarding diffusion of corrosive species such as oxygen.

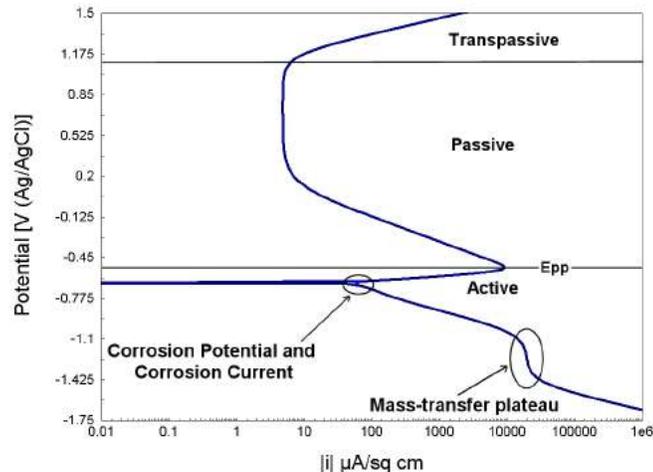


Figure 3. Basic polarization curve. At a potential given by  $E_{pp}$ , the metal will begin to express passive behavior.

The type of curve predicted by OLI Studio: Corrosion Analyzer, in the active-to-passive region is one that can only be produced with a potentiostatic controlled experiment or a galvanostatic controlled experiment. In a potentiostatic experiment, the potential (or more correctly polarization) is varied and current is measured. In a galvanostatic experiment the current is varied, and the potential is measured. Figure 4 shows a net current curve that would be produced by a galvanostatic experimental technique. When plotted, the passive region would be skipped all-together, and only the active and trans-passive regions would appear. However, if the experiment was reversed in the trans-passive region, the passive region could be seen, but the return to the active region would be missed. This is the same system/curve shown in Figure 4.

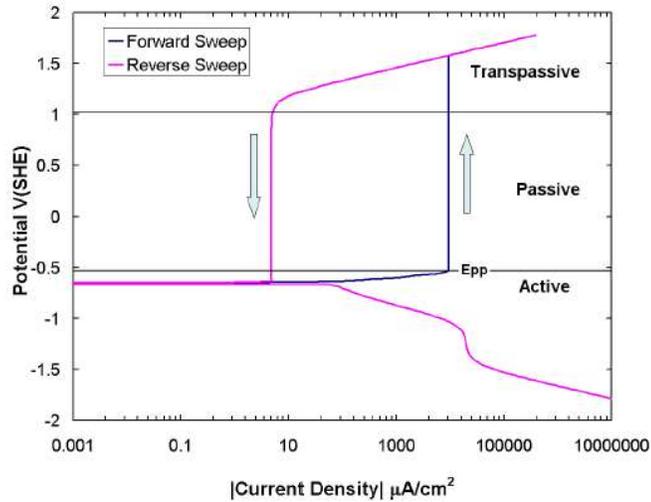


Figure 4. Basic polarization curve demonstrating a galvanostatic sweep. The arrows indicate how the potential is changing as one moves along the line.

The point at which the active/passive transition is made can be seen by the potential “jump” made by the small increase in current density at the point labeled “E<sub>pp</sub>.” The passive current density and the transition from passive to transpassive behavior is seen with the current density sweep is reversed and slowly brought back to zero. What is missed, is the transition region from the active corrosion rate and the passive corrosion rate.

### Transpassive Region

As the potential is increased to a high anodic value, other anodic reactions may become substantial enough to affect the net current. The transpassive region is the section of the curve anodic to the corrosion potential where the current density increases again after having been flat for a range of potential. In the case of the curve plotted in Figure 5, the reaction is the oxygen evolution reaction for the breakdown of water. In other words, the water stability limit is reached.

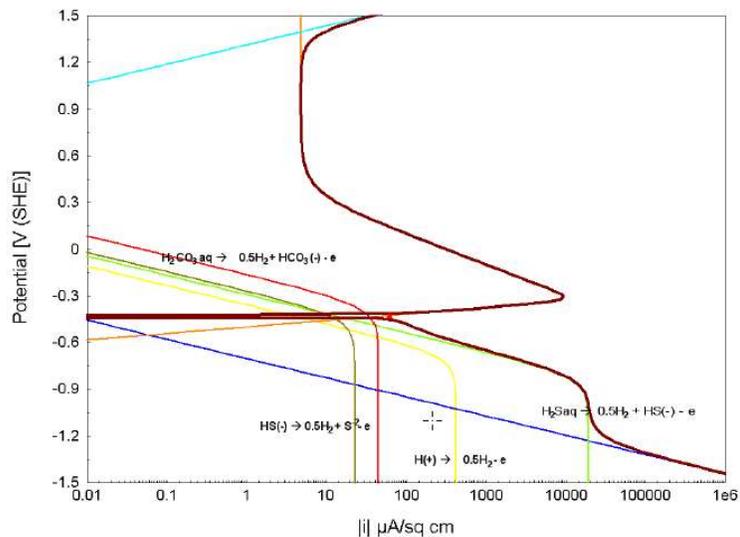


Figure 5. Polarization curves for carbon steel in an environment saturated with CO<sub>2</sub> and H<sub>2</sub>S.

## pH Changes at the Interface

It is commonly observed that the pH at the metal surface increases from the bulk pH. The partial processes shown in the polarization curves explain the behavior.

Figure 5 shows three reactions where hydrogen ions are consumed at the metal surface, and none are produced. As the mass transfer limitation is approached, the pH will rise because fresh hydrogen ions will not be able to diffuse fast enough to replace what is lost through the partial processes.

## Fluid Dynamics

As seen so far, the corrosive species must come from the bulk aqueous phase before it can react at the metal surface. Equation 8 shows that the fluid velocity plays an important role in determining the rate at which a species that influences corrosion can get to the surface. Therefore, understanding how fluid dynamics affects corrosion is important.

Examining equation 8 shows that a known fluid velocity profile is needed, or simultaneous solution of Navier-Stokes, mass conservation, and equation 8 is needed. Since it is computationally expensive to solve all three systems of equations, OLI uses known solutions for certain velocity profiles to determine  $i_{lim}$ . These are:

- Static -  $v \approx 0$
- Pipe flow
- Rotating disk
- Rotating cylinder
- Complete agitation – a special limiting case where no mass-transfer-limitations
- Defined shear stress
- Approximate multiphase flow

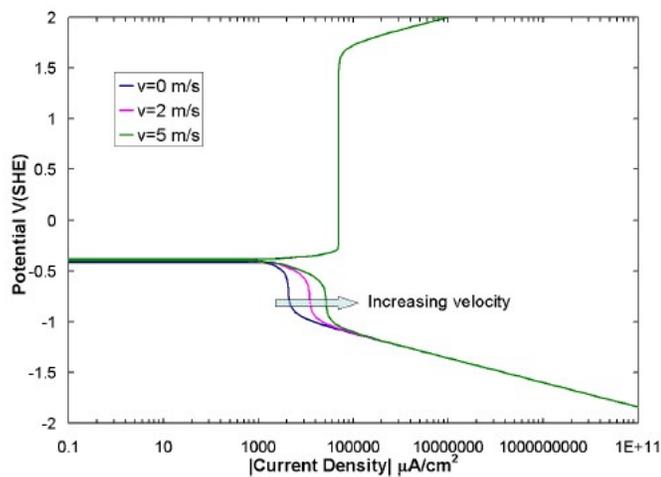


Figure 6. Net current density curve for the same system at three different velocities

Figure 6 shows a system where only the velocity has been varied. The mass-transfer-limited plateau increases with increasing velocity indicating the greater availability of species due to increased mass transport.

## A Basic General Corrosion Rate Calculation

A brief introduction to the corrosion rate tool will be shown in the example below. As we go through the example, the basic definitions, functionalities and reporting for the *Corrosion rate* tool will be introduced.

### Corrosion rate of an oxygenated 0.1 m NaCl solution

#### Starting the Simulation



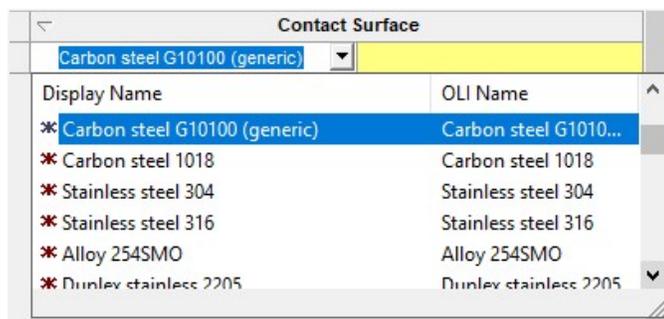
- ✓ To start the software, double-click the OLI Studio icon on the desktop, which will take you to the OLI Studio interface where you can start creating your calculations.

Use the inputs and parameters from the table below to create the stream's composition. Certain inputs, such as the name style, units, etc. will require further adjustments, and will be described as necessary.

Corrosion Rate Calculation			
Calculation Settings		Stream Composition and Conditions	
Stream Name	CR of carbon steel	Stream Amount	Calculated
Name Style	Display Formula	Temperature	25 °C
Unit Set	Metric, Batch, Moles	Pressure	1 atm
Framework	AQ	H2O	55.5082 moles
Calculation Type	Corrosion Rates	O2	2.5e-4 moles
Contact Surface	Carbon Steel G10100 (generic)	NaCl	0.1 moles

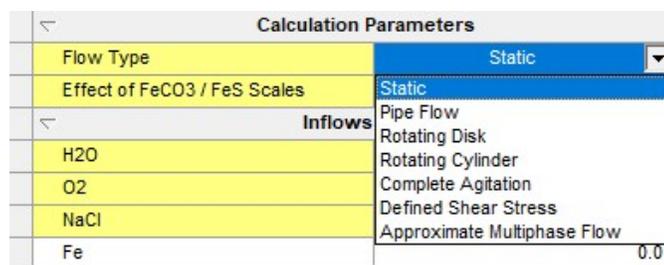
- ✓ Add a new **Stream**
- ✓ **Click** on the new Stream and press **<F2>** to change the name to *CR of carbon steel*
- ✓ Select the **AQ** thermodynamic Framework
- ✓ **Click** on the **Names Manager** Icon and select the **Formula** option
- ✓ **Click** on the **Units Manager** Icon, and select Metric, Batch, Moles
- ✓ Enter the composition, temperature and pressure of the stream given in the table above
- ✓ Go to the **Add Calculation** button and select **Corrosion Rates** calculation or by selecting the **Add Corrosion Rates** icon in the Actions Pane. Your screen should look like the image below.

**Note:** By default, the software has selected **Carbon steel G10100 (generic)** as the default contact surface to perform the corrosion rates on. You can click on the white space of the **Carbon steel G10100 (generic)** name, and it will show a drop-down arrow. You can then click on the dropdown arrow, and you will be able to see and select any alloy present in the **Alloy** database.



Additionally, the **Calculation Parameters** grid shows two options: (1) Flow Type and (2) Effect of FeCO<sub>3</sub> /FeS scales on corrosion rates.

By default, the software selects **Static** as **Flow Type**. There are 7 options for Flow Type, and a brief description of the first five options will be given below.



#### *Static*

The solution is not flowing in this calculation.

#### *Pipe Flow*

The fluid is flowing through a pipe. The pipe diameter and flow velocity must be defined. The default pipe diameter is 0.1 meters and the default flow velocity is 2 m/s.

#### *Rotating disk*

This reproduces a type of experiment that is used quite frequently in the laboratory. A disk is rotated to bring fluid to the surface of the electrode in a predictable manner. The diameter of the disk is specified as well as the revolutions per minute (RPM). The default diameter is 0.01 meters and the default RPM is 5000 RPM.

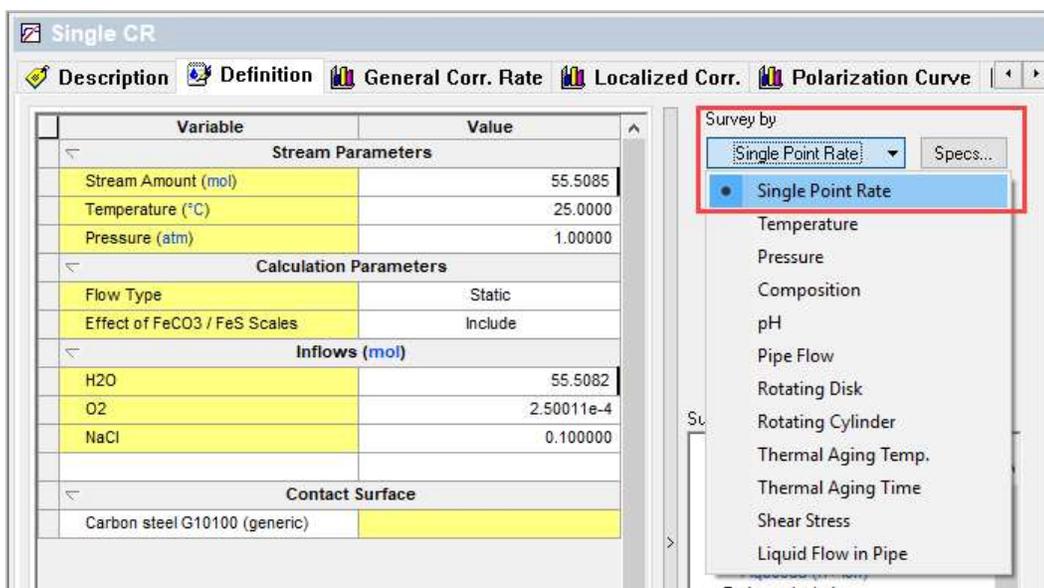
#### *Rotating Cylinder*

This reproduces a type of experiment that is used quite frequently in the laboratory. A cylindrical rotor is rotated to bring fluid to the surface of the electrode in a predictable manner. The diameter of the rotor is specified as well as the revolutions per minute (RPM). The default diameter is 0.01 meters and the default RPM is 5000 RPM.

#### *Complete Agitation*

In this calculation, the liquid phase is completely agitated, and no mass transfer limitations apply.

- ✓ Leave the default alloy **Carbon steel G10100 (generic)** as the contact surface
- ✓ **Go to the Survey by option and select Single Point Rate.** This option will allow you to calculate the corrosion rate at the temperature and pressure specified.



**Note:** You can also study the effect of other variables such as temperature, pressure, (chemical species) composition, pH, pipe flow, etc. on the corrosion rate. The effect of these variables can be set up as a survey calculation. In the upcoming corrosion rate examples, survey calculations to study corrosion rates will be shown in more detail.

A brief description of the most common survey types for studying corrosion rates are given below.

*pH Survey* – This calculation is similar to the pH survey available in OLI Studio: Stream Analyzer. The specification requires a titrant acid and base to change the pH.

*Temperature Survey* – The default range is from 25-100 °C. Any range may be used by changing the Range option. The user should consider that some points in the survey may not converge due to phase changes (e.g., boiling off of aqueous liquids).

*Composition Survey* – The composition of a chemical compound, for example NaCl, can be varied to study its effects on corrosion rates. The range of the chemical compound defaults from 0 to 1 mole with an increment of 0.1 moles. This range can be changed via the Range option.

Care should be taken when adding salts that can form hydrates (e.g.,  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ ). When these hydrated salts begin to precipitate from solution, large amounts of water may be complexed with the crystal. The solution may dehydrate, and non-convergence may be the result.

*Pressure Survey* – The pressure of the system can also be varied. The default range can be changed via the Range option. Care should be taken when working at very low pressures since the solution may inadvertently boil off the liquid and non-convergence may result.

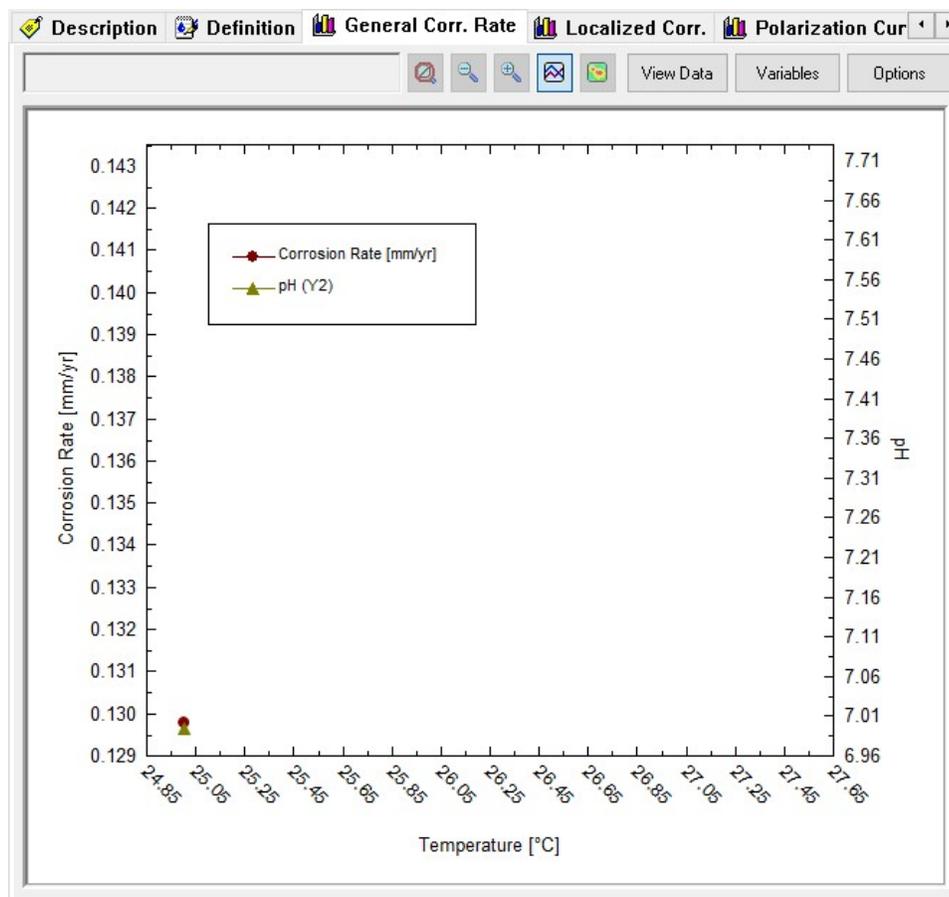
*Flow Velocity Survey* – In systems that are flowing, the flowrate of the stream can be varied.

- ✓ Now, we are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key

- ✓ It is time to **save** your file (**File > Save as...**) or using the **save** icon in the tool bar. Create a new file and name it: *Corrosion Rates*.

## Analyzing the Results

- ✓ Click on the **General Corr. Rate** tab (  **General Corr. Rate** ). This tab displays a plot showing the results of corrosion rate and pH.

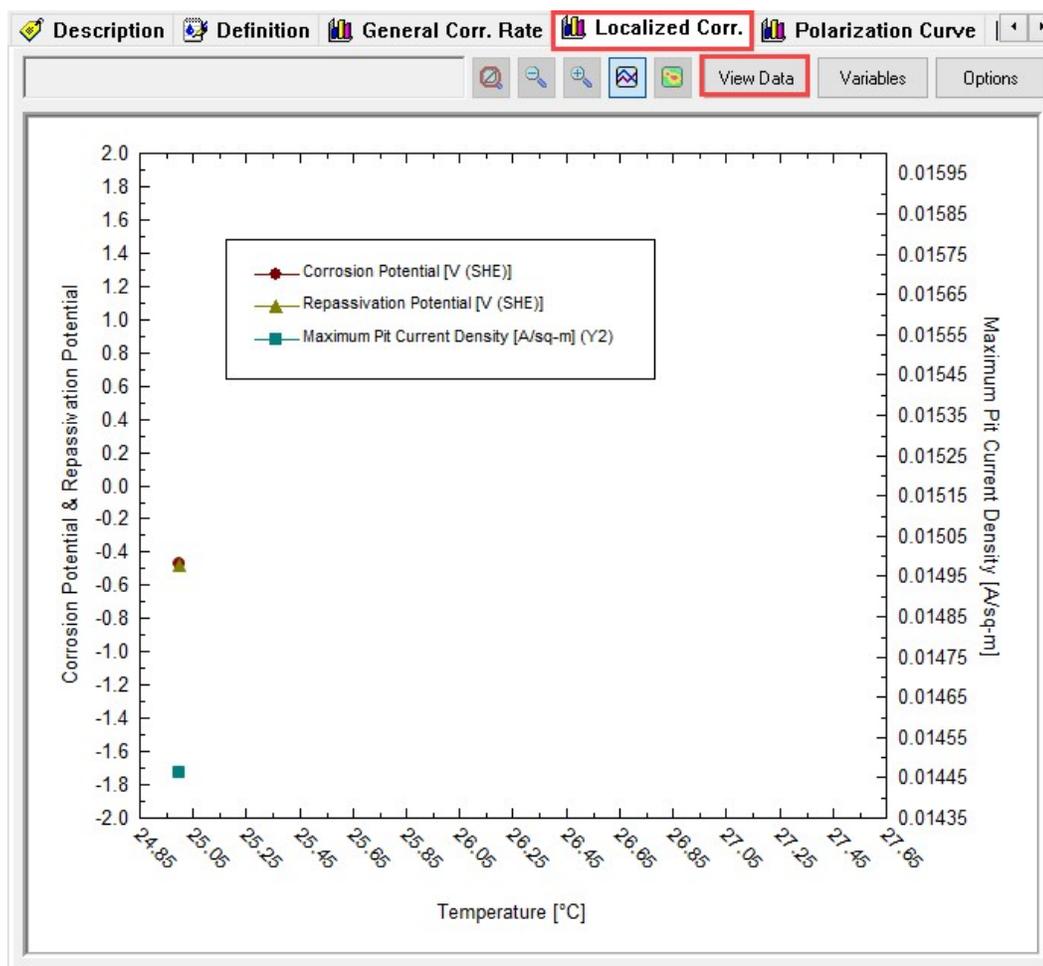


- ✓ **Click** on the **View Data** button to see the results in tabulated form.

	Temperature	Corrosion Rate	pH
	°C	mm/yr	
1	25.0000	0.129801	6.99516

The predicted corrosion rate of carbon steel at 25 °C and 1 atm is ~0.13 mm/year when exposed to an oxygenated 0.1 m NaCl solution. It is important to highlight that this predicted corrosion rate is the corrosion rate once the system has reached a steady state.

- ✓ Click on the **Localized Corr. Rate** tab (Localized Corr.). This tab displays a plot showing the results of three different calculated data:
  - Corrosion Potential (red dot)
  - Repassivation Potential (yellow triangle)
  - Maximum Pit Current Density (blue square)

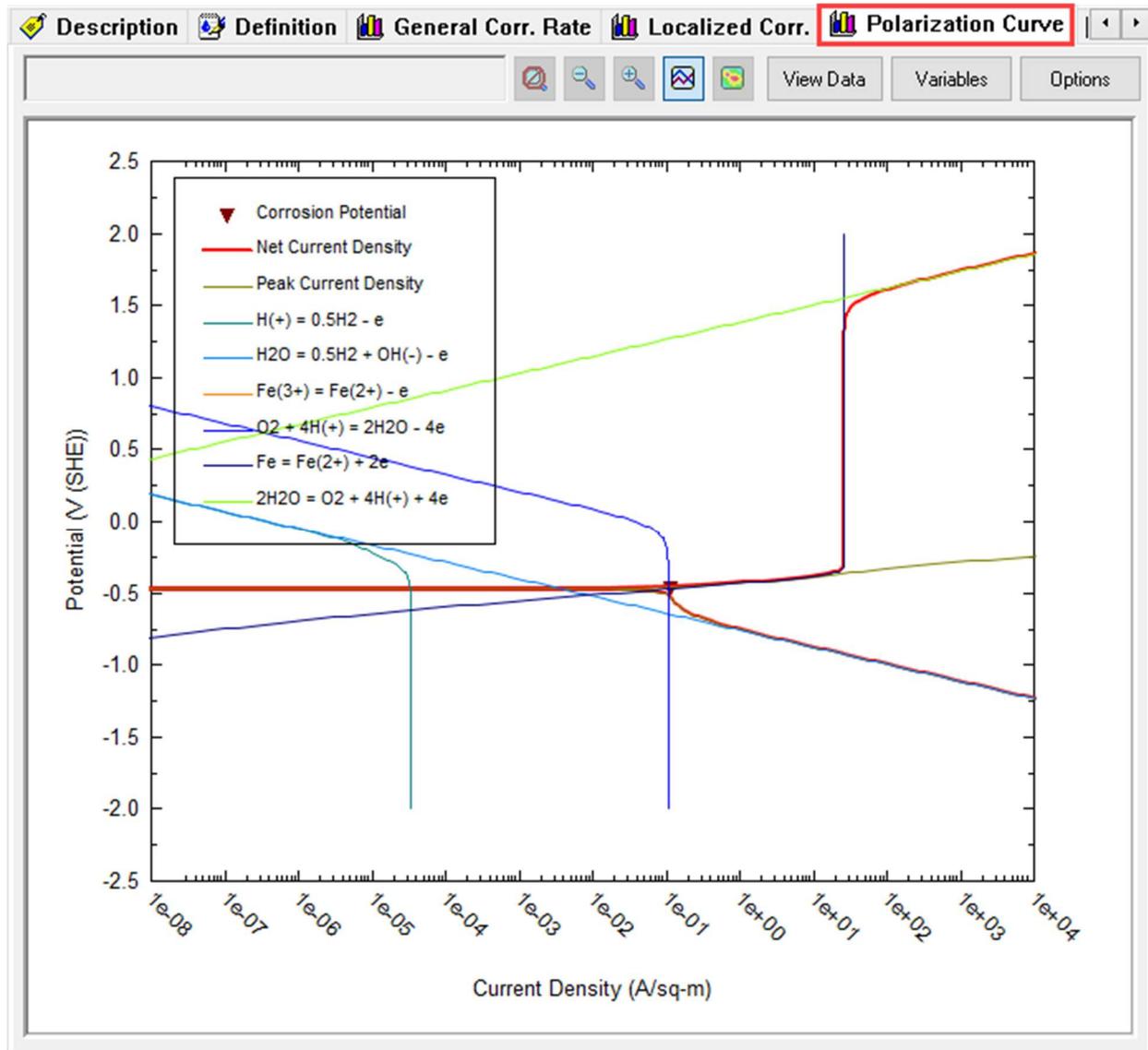


- ✓ Click on the **View Data** button to see the results in tabulated form.

	Temperature	Corrosion Potential	Repassivation Potential	Maximum Pit Current Density
	°C	V (SHE)	V (SHE)	A/sq-m
1	25.0000	-0.472418	-0.481902	0.0144636

Notice that in this case, the corrosion potential has a higher value than the repassivation potential. This indicates that carbon steel at 25 °C and 1 atm when exposed to an oxygenated 0.1 m NaCl solution will likely suffer localized corrosion (pitting or crevice corrosion). The maximum pit current density gives the worst-case pitting rate for these conditions.

- ✓ Now, click on the **Polarization Curve** tab (  **Polarization Curve** ). This tab displays a plot showing the calculated polarization curve of carbon steel.



The net polarization curve is given by the red curve. This red curve is obtained by adding up all the currents of the half reactions at a given potential. The corrosion potential is calculated by applying the mixed potential theory, and it is represented by this red triangle. Once the corrosion potential is obtained, the corrosion current density also is computed and subsequently the corrosion rate.

# Gas condensate corrosion – Understanding the Polarization Curve

## Condensed overhead gas and mitigation strategies

An alkanolamine gas sweetening plant has corrosion problems in the condensed overhead gas.

Diethanolamine is used to neutralize an acid gas containing carbon dioxide (CO<sub>2</sub>) and hydrogen sulfide (H<sub>2</sub>S). The diethanolamine is regenerated and the acid gases are driven off in a stripper. The off gas from this stripper is saturated with water vapor. As these gases cool, they will condense. This condensate can be very corrosive. The plant's service life can be shortened considerably due to these condensed acid gases.

In this example, you will calculate the gas dew point temperature, remove the condensed aqueous phase and perform a Corrosion Rate calculation with the condensed water. Lastly, you will consider mitigation strategies for the pipes.

You are introducing *fluid velocity* and *liquid condensation* into the calculation. The software uses a diffusion layer model to compute mass transfer to and from corroding surfaces. Higher rates produce thinner layers, resulting in faster mass transfer rates, and thus higher corrosion rates. The liquid condensation point is straightforward; it calculates the temperature (or pressure) where the first liquid drop forms.

## Starting the Simulation

Use the inputs and parameters from the table below to create the stream's composition. Certain inputs, such as the name style, units, etc. will require further adjustments, and will be described as necessary.

Corrosion Rate Calculation			
Calculation Settings		Stream Composition and Conditions	
Stream Name	Gas condensate	Stream Amount	1e5 moles
Name Style	Display Formula	Temperature	38 °C
Unit Set	Metric, Batch, Mole Fraction	Pressure	1.2 atm
Framework	AQ	H2O	Calculated (mole%)
Calculation Type	Corrosion Rates	CO2	77.4
Survey	Single Point Rate	N2	0.02
Flow Type	Pipe Flow	H2S	16.6
Pipe Diameter	10 cm	CH4	0.5
Pipe Flow Velocity	2 m/s	C2H6	0.03
Contact Surface	Carbon Steel G10100 (generic)	C3H8	0.03

- ✓ Add a new **Stream**
- ✓ **Click** on the new Stream and press **<F2>** to change the name to *Gas Condensate*
- ✓ Select the **AQ** thermodynamic Framework
- ✓ **Click** on the **Names Manager** Icon and select the **Formula** option
- ✓ **Click** on the **Units Manager** Icon, and select Metric, Batch, Mole Fraction
- ✓ Enter the composition, temperature and pressure of the stream given in the table above
- ✓ Go to the **Add Calculation** button and select **Corrosion Rates** calculation or by selecting the **Add Corrosion Rates** icon in the Actions Pane.
- ✓ **Go** to the **Survey by** option and select **Single Point Rate**. Change the name to **Gas Cond. Dew Point**.

- ✓ **Change** the Flow Type from Static to **Pipe Flow**.
- ✓ **Specify** the **Pipe Diameter** = 10 cm and the **Pipe Flow Velocity** = 2 m/s.
- ✓ Leave the default alloy **Carbon steel G10100 (generic)** as the contact surface

Your screen should look like the image below.

The screenshot shows the OLI Studio interface with the 'Rates' window open. The 'Rates' window has several tabs: 'Definition', 'General Corr. Rate', 'Localized Corr.', 'Polarization Curve', and 'Report'. The 'Definition' tab is active, showing a table of parameters and their values.

Variable	Value
<b>Stream Parameters</b>	
Stream Amount (mol)	1.00000e5
Temperature (°C)	38.0000
Pressure (atm)	1.20000
<b>Calculation Parameters</b>	
Calculate	Temperature
Flow Type	Pipe Flow
Pipe Diameter (cm)	10.0000
Pipe Flow Velocity (m/s)	2.00000
Effect of FeCO <sub>3</sub> / FeS Scales	Include
<b>Inflows (mole %)</b>	
H <sub>2</sub> O	5.42000
CO <sub>2</sub>	77.4000
N <sub>2</sub>	0.0200000
H <sub>2</sub> S	16.6000
CH <sub>4</sub>	0.500000
C <sub>2</sub> H <sub>6</sub>	0.0300000
C <sub>3</sub> H <sub>8</sub>	0.0300000
Fe	0.0
<b>Contact Surface</b>	
Carbon steel G10100 (generic)	

On the right side of the 'Rates' window, there is a 'Summary' section with the following information:

- Unit Set: Metric (mole fraction)
- Automatic Chemistry Model: Aqueous (H+ ion) Databanks: Corrosion (A.Q), Aqueous (H+ ion)
- Redox selected: Using K-fit Polynomials, T-span: 25.0 - 225.0, P-span: 1.0 - 1500.0
- Dew Point Calculation: 1.20000 atm, 37.5851 °C
- Calculation complete
- Single Point: No secondary survey selected
- Polarization Curve Range: Range -2.0 to 2.0 V (SHE), Step size 0.01 V (SHE), No. steps 400

Now that the gas condensate stream is created, the next task is to isolate the condensed water at the dew point temperature.

- ✓ **Click** on the **Specs** button. This will open a new window
- ✓ Under the **Category** section, select **Calculation Type**
- ✓ Change the Type of Calculation from Isothermal to **Dew Point**. Make sure that radio button for temperature is selected since we are going to calculate the Dew Point temperature for this example. Then click **OK**.
- ✓ Now, we are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key
- ✓ It is time to **save** your file (**File > Save as...**) or using the **save** icon in the tool bar. You can save it under the same file created in the previous example named *Corrosion Rates*.

## Analyzing the Results

✓ Click on the **General Corr. Rate** tab (  **General Corr. Rate** ).

✓ **Click** on the **View Data** button to see the results in tabulated form.

	Temperature	Corrosion Rate	pH
	°C	mm/yr	
1	37.5851	0.704502	3.92719

✓ Notice that the calculated dew temperature is 37.6°C, corrosion rate is 0.7 mm/year, and the dew point pH is 3.9. To further interpret the results of this calculation, we are going to study the polarization curve.

✓ Click on the **Polarization Curve** tab (  **Polarization Curve** ). Before interpreting this plot, we will format it for easy viewing.

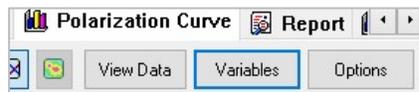
✓ Click on the **Options** button. This will open a new window.



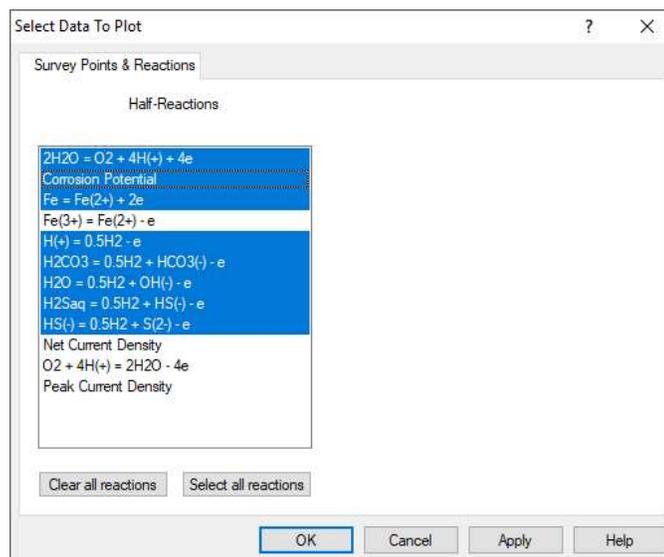
✓ Under the **Category** section select **X axis**. Change the **Minimum** to 1e-6 and **Maximum** to 1e6.

✓ Now, select **Y axis**. Change the **Minimum** to -1.5 and **Maximum** to 1.5. Then **click OK**.

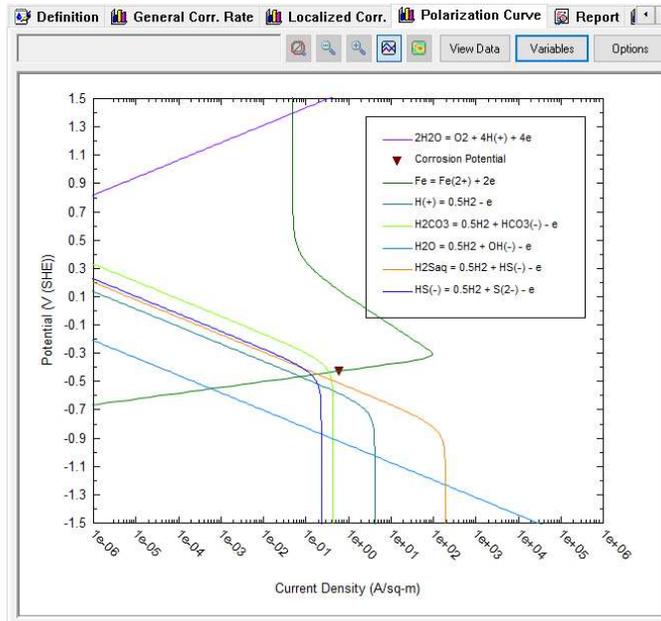
✓ Click on the **Variables** button. This will open a new window.



✓ Remove the following variables by unchecking them. See image below. Then **Click OK**.



✓ Your polarization curve should look like the image below.



You can click and drag the legend of the polarization curve to your desired position.

This is a measured potential vs. current density plot. The anodic portion (**green curve**) is the carbon steel. There are cathodic reactions. The sum of the cathodic currents adds up to the anode curve at a single point: The corrosion potential (represented by the inverted red triangle ▼) with a value of -0.43 V vs SHE. At the corrosion potential, the anodic and cathodic currents are equal, and this value is also known as the  $i_{\text{corr}}$ . For this example,  $i_{\text{corr}}=0.61 \text{ A/m}^2$ .

Notice that the cathodic reaction that contributes the most to corrosion is  $\text{H}_2\text{CO}_3$  (**light green line**). The next contributors are  $\text{H}_2\text{S}$  (**orange line**) and  $\text{HS}^-$  (**blue line**) equally. After that is  $\text{H}^+$  (**turquoise line**). Water reduction (**light blue line**), contributes the least to corrosion.

### Mitigation Strategies

There are several mitigating solutions to this corrosion problem.

One is adding insulation to prevent temperature drops. The dew point is very close to the overhead gas temperature so this may not be a suitable option. Adding heat to keep the temperature above the dew point is usually considered along with insulation.

Changing the chemistry to change the partial oxidation and reduction processes is also an option.

Changing alloys could mitigate the corrosion problems as well.

We will explore the change of chemistry and change of alloys for this example.

## Adjusting the solution chemistry

The condensate pH is approximately 3.9. We can try to add a base to increase the pH. In this section, we will add Diethanolamine to raise the pH to 7.5.

### Single Point– Set pH Calculation

- ✓ Click on the 'Gas Condensate' stream and go to the **Add Calculation** button and select **Single Point** calculation or by selecting the **Add Single Point** icon in the Actions Pane.
- ✓ Change the name to **DEA** using the <F2> key.
- ✓ Add **DEA** in the inflows grid. (It should have changed to the formula name: HN(C2H4OH)2)
- ✓ Go to the **Type of Calculation** option and select **Set pH**
- ✓ Change the **Target pH** to 7.5
- ✓ Click on the drop-down arrow for the pH Base Titrant and select DEA (or HN(C2H4OH)2)

We have set up the calculation to adjust the amount of DEA to match the target value of pH=7.5.

Your screen should look like the image below.

The screenshot shows the OLI Studio interface for a calculation named 'DEA'. The main window contains a table with the following data:

Variable	Value
<b>Stream Parameters</b>	
Stream Amount (mol)	1.00000e5
Temperature (°C)	38.0000
Pressure (atm)	1.20000
<b>Calculation Parameters</b>	
Target pH	7.50000
Use Single Titrant	No
pH Acid Titrant	HCL
pH Base Titrant	HN(C2H4OH)2
<b>Inflows (mole %)</b>	
H2O	5.42000
CO2	77.4000
N2	0.0200000
H2S	16.6000
CH4	0.500000
C2H6	0.0300000
C3H8	0.0300000
HN(C2H4OH)2	0.0

The right-hand panel shows the 'Type of calculation' set to 'Set pH' and a 'Calculate' button. The 'Summary' panel indicates the calculation is not done.

- ✓ Now, we are ready to perform the calculation. Click on the **Calculate** button or press the <F9> key
- ✓ It is time to **save** your file (**File > Save as...**) or using the **save** icon in the tool bar. You can save it under the same file created in the previous example named *Corrosion Rates*.

## Analyzing the Results

- ✓ Check the summary box to analyze the results.

Summary

Unit Set: Metric (mole fraction)

Automatic Chemistry Model  
 Aqueous (H+ ion) Databanks:  
 Aqueous (H+ ion)  
 Using K-fit Polynomials  
 T-span: 25.0 - 225.0  
 P-span: 1.0 - 1500.0

Set pH Calculation  
 38.0000 °C  
 1.20000 atm  
 Target pH 7.50000  
 Acid Titrant: HCl  
 Total: 0.0 mole %  
 Base Titrant: HN(C2H4OH)2  
 Total: 5.96844e-4 mole %  
 Added: 5.96844e-4 mole %

Phase Amounts  
 Aqueous 31.6062 mol  
 Vapor 99968.5 mol  
 Solid 0.0 mol

Aqueous Phase Properties  
 pH 7.50001  
 Ionic Strength 0.0160370 mol/mol  
 Density 1.02648 g/ml

The pH is set to 7.5 and the inflow of DEA to the total gas is approximately 5.97e-4 mole%.

The DEA concentration in the condensing water and the amount remaining in the vapor phase can both be viewed in the Report tab.

- ✓ Click on the **Report Tab** and go to the **Total and Phase Flows** and **Species Output** tables

### Total and Phase Flows (Amounts)

column Filter Applied: Only Non Zero Values

	Total	Aqueous	Vapor
	mol	mol	mol
Mole (True)	1.00000e5	31.6062	99968.5
Mole (App)	1.00001e5	32.0477	99968.5
	g	g	g
Mass	4.08064e6	642.188	4.08000e6
	L	L	L
Volume	2.11456e6	0.625619	2.11456e6

### Species Output (True Species)

Row Filter Applied: Only Non Zero Values

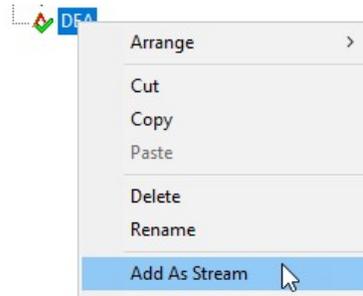
column Filter Applied: Only Non Zero Values

	Total	Aqueous	Vapor
	mole %	mole %	mole %
CO2	77.3994	0.0416672	77.4239
H2S	16.5999	0.0271211	16.6052
H2O	5.41962	96.6827	5.39076
CH4	0.499999	1.37153e-5	0.500157
C2H6	0.03	9.08534e-7	0.0300094
C3H8	0.03	7.06434e-7	0.0300094
N2	0.02	2.56549e-7	0.0200063
NH2(C2H4OH)2(+1)	5.02996e-4	1.59145	
HCO3-1	3.689e-4	1.16718	
C5H10NO4-1	6.87352e-5	0.217474	
HS-1	5.7612e-5	0.182281	
HN(C2H4OH)2	2.51153e-5	0.0778779	5.01249e-7
CO3-2	3.86988e-6	0.0122441	
S-2	3.93925e-9	1.24636e-5	
OH-1	6.55471e-10	2.07387e-6	
H+1	2.47871e-11	7.8425e-8	
Total (by phase)	100.0	100.0	100.0

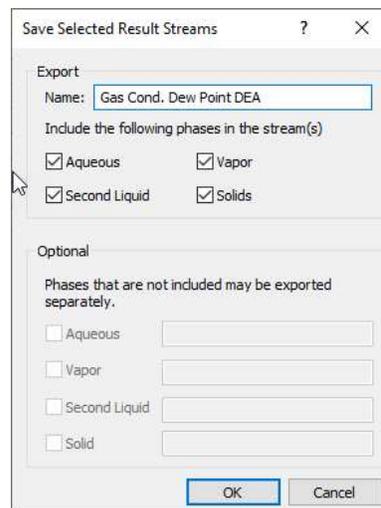
Recalculating the corrosion rate with DEA

We now can recalculate the corrosion rate with DEA in the stream. This represents some DEA entrained in the vapor phase in the gas that leaves the regenerator.

- ✓ **Right click** on the **DEA** Stream, and select the option **Add As Stream**

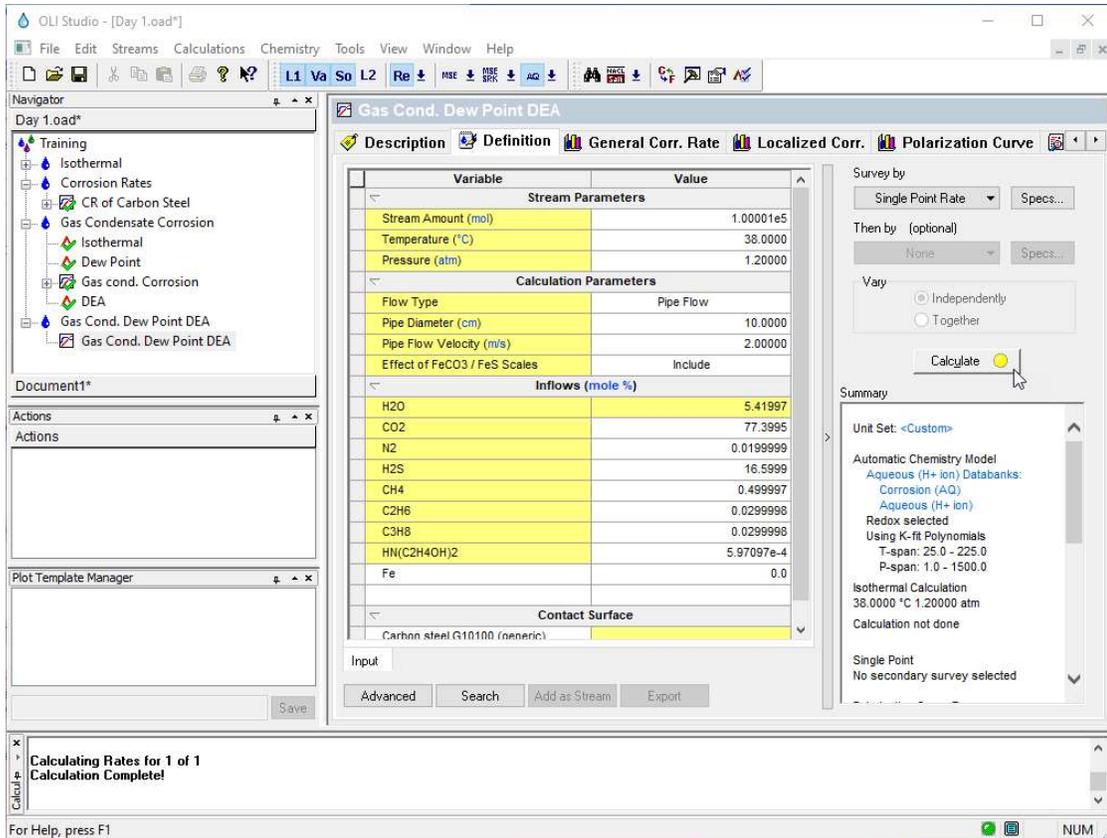


- ✓ This will open a new window
- ✓ Change the name to **Gas Cond. Dew Point DEA** and click **OK**



- ✓ Click on **the Gas Cond, Dew Point DEA** stream
- ✓ Add a **corrosion rate** calculation
- ✓ Select **single point rate**
- ✓ Change **Flow Type** to **Pipe Flow** (Leave the default values of pipe diameter= 10 cm and pipe flow velocity of 2 m/s)
- ✓ Change the name to **Gas Cond. Dew Point DEA**
- ✓ Leave the default alloy **Carbon steel G10100 (generic)** as the contact surface

Your screen should look like the image below.



- ✓ Now, we are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key
- ✓ It is time to **save** your file (**File > Save as...**) or using the **save** icon in the tool bar. You can save it under the same file created in the previous example named *Corrosion Rates*.

### Analyzing the Results

- ✓ Click on the **General Corr. Rate** tab ( General Corr. Rate ).
- ✓ **Click** on the **View Data** button to see the results in tabulated form.

	Temperature	Corrosion Rate	pH
	°C	mm/yr	
1	38.0000	0.480600	7.50000

Notice that the corrosion rate has decreased from 0.7 mm/year to 0.48 mm year. The pH is 7.5 - the target pH. Based on these results neutralizing the pH had a partial effect on corrosion reduction.

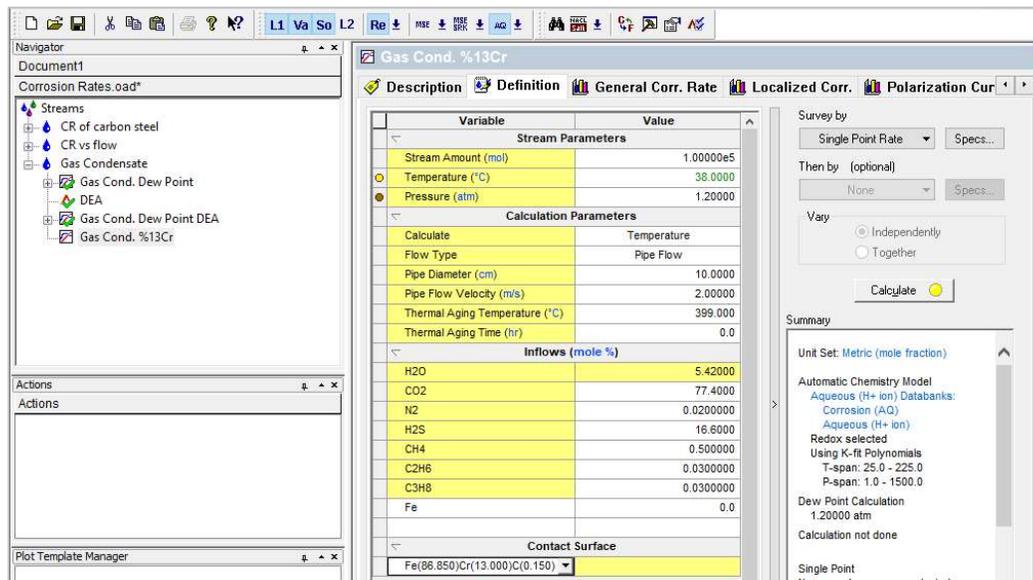
### Changing the Alloy

Since treating the acid gas with a base is probably not a good idea for metal hydroxides, perhaps we can change the alloy. We will add a new corrosion rates calculation and test different alloys.

## 13%Cr Stainless Steel

1. **Copy** 'Gas Cond. Corrosion' corrosion calculation, and **paste** it under the stream 'Gas Condensate'
2. Change the name to **Gas Cond. Corrosion - 13Cr** using the <F2> key.
3. **Change the contact surface to 13%Cr stainless steel**

Your screen should look like the image below.



4. Now, we are ready to perform the calculation. **Click** on the **Calculate** button or press the <F9> key
5. It is time to **save** your file (**File > Save as...**) or using the **save** icon in the tool bar. You can save it under the same file created in the previous example named *Corrosion Rates*.

## Analyzing the Results

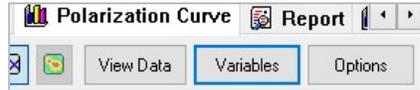
- i. Click on the **Report** tab to see the results. (You may need to use the ◀▶ buttons to move the tabs and find the Report tab).
- ii. Go to the **Calculated Rates** table

Calculated Rates		
Corrosion Rate	0.0622463	mm/yr
Corrosion Potential	-0.314266	V (SHE)
Repassivation Potential	>2.0	V(SHE)
Corrosion Current Density	0.0566434	A/sq-m

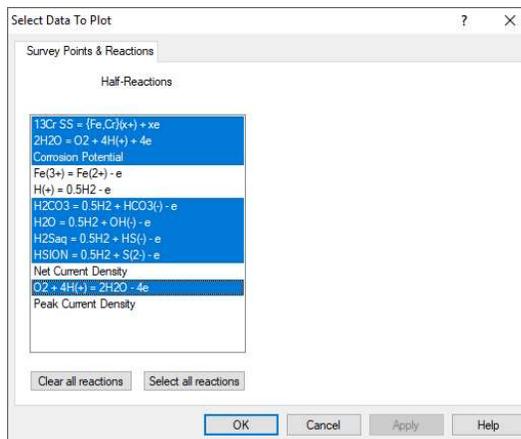
The corrosion rate of 13%Cr is one order of magnitude lower when compared to the corrosion rate for Carbon Steel, i.e. at 0.06 mm/year for 13%Cr vs 0.7 mm/year for Carbon Steel. This is consistent with the use of 13% Cr to protect against CO<sub>2</sub> corrosion.

iii. Click on the **Polarization Curve** tab (  Polarization Curve ).

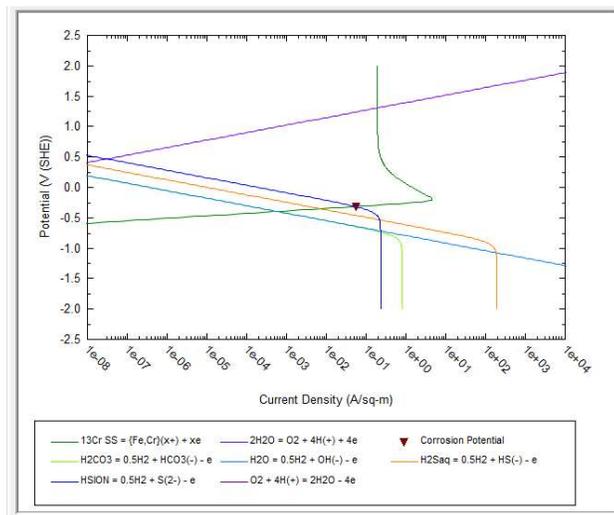
iv. Click on the **Variables** button. This will open a new window.



v. Remove the following variables by unchecking them. See image below. Then **Click OK**.



vi. The polarization curve (after some layout modifications) should look like the image below.



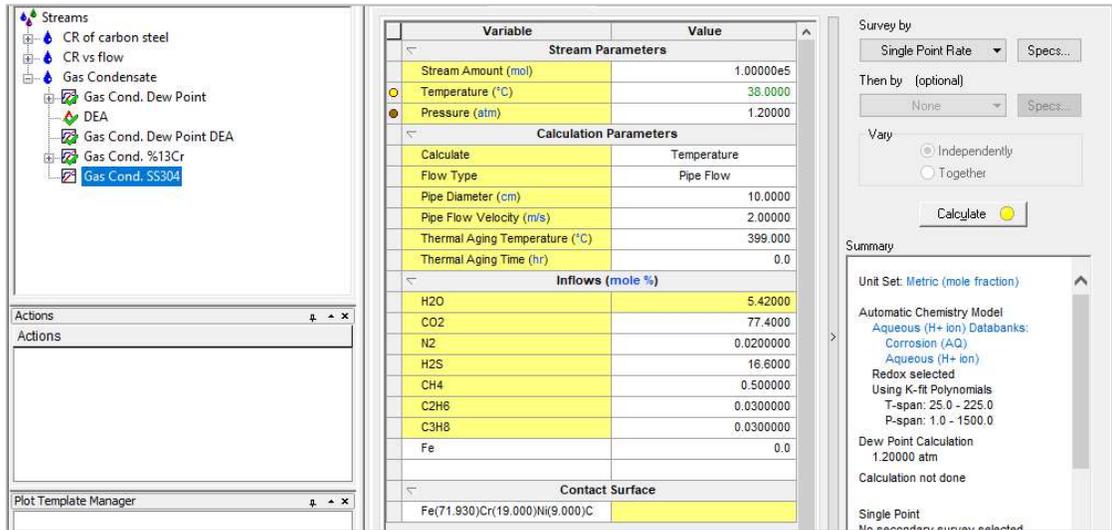
The layout of the plot was changed for easy reading. To change layout, you can right click on any part of the plot and select the option *Alloy Layout Changes* to modify the appearance of your plot.

The corrosion potential of 13%Cr is -0.31 V vs SHE and the corresponding corrosion current  $i_{\text{corr}}=0.06 \text{ A/m}^2$ . The  $i_{\text{corr}}$  for Carbon Steel was  $0.61 \text{ A/m}^2$ , this means that 13%Cr is 10x more resistant to corrosion under the same conditions.

## Stainless Steel 304

- ✓ **Copy** 'Gas Cond. Corrosion' corrosion calculation, and **paste** it under the stream 'Gas Condensate'
- ✓ Change the name to **Gas Cond. Corrosion - 13Cr** using the **<F2>** key.
- ✓ **Change** the **contact surface** to **Stainless Steel 304**

Your screen should look like the image below.



- ✓ Now, we are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key
- ✓ It is time to **save** your file (**File > Save as...**) or using the **save** icon in the tool bar. You can save it under the same file created in the previous example named *Corrosion Rates*.

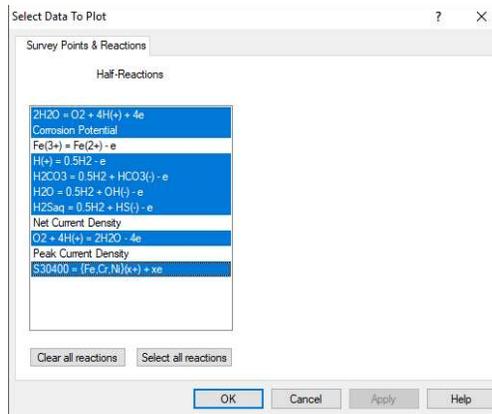
## Analyzing the Results

- ✓ Click on the **Report** tab to see the results. (You may need to use the ◀▶ buttons to move the tabs and find the Report tab).
- ✓ Go to the **Calculated Rates** table

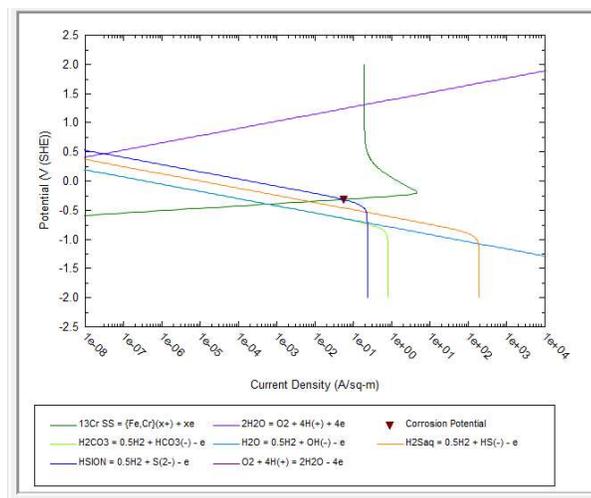
Corrosion Rate	3.57108e-3	mm/yr
Corrosion Potential	-0.172583	V (SHE)
Repassivation Potential	>2.0	V(SHE)
Corrosion Current Density	3.29499e-3	A/sq-m

The corrosion rate of 304 SS is now 0.0036 mm/year. This is a negligible value.

- ✓ Click on the **Polarization Curve** tab (📊 Polarization Curve).
- ✓ Click on the **Variables** button. This will open a new window.
- ✓ Remove the following variables by unchecking them. See image below. Then **Click OK**.



The polarization curve (after some layout modifications) should look like the image below.



The layout of the plot was changed for easy reading. To change layout, you can right click on any part of the plot and select the option Alloy Layout Changes to modify the appearance of your plot.

The corrosion potential of SS304 is -0.17 V vs SHE and the corresponding corrosion current  $i_{\text{corr}}=3.3\text{e-}3 \text{ A/m}^2$ . With this low corrosion current density, sour gas regeneration can be remedied using a higher-grade alloy such as SS304.

## Chapter IV – Repassivation Potential and Localized Corrosion

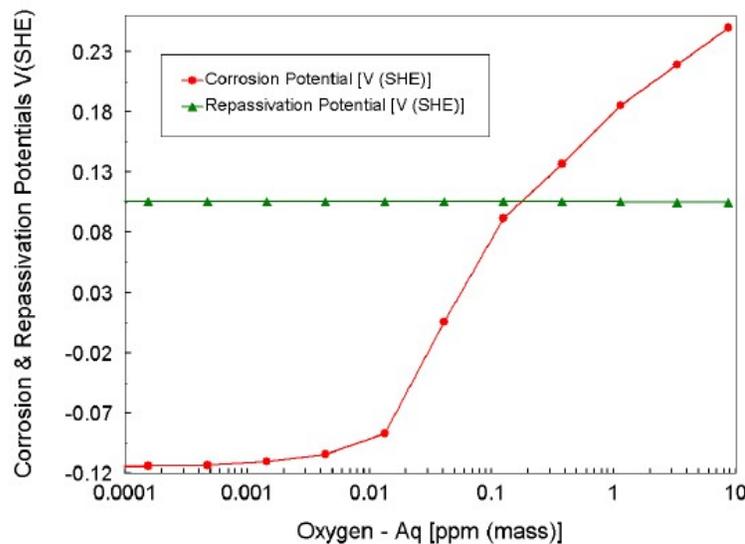
The OLI Studio: Corrosion Analyzer, includes the ability to predict the repassivation potential and a peak current density for active pits. The repassivation potential is important for corrosion analysis because it indicates how well an alloy can “repassivate” active pits.

### Repassivation Potential

The repassivation Potential ( $E_{rp}$ ) also called the protection potential. The repassivation potential is a measure of the tendency of an alloy to undergo localized corrosion in a given environments. The underlying justification for the use of  $E_{rp}$  is the fact that, for engineering applications, only the fate of stable pits or crevices is important. Pits that nucleate, but do not grow beyond an embryonic stage (also known as metastable pits) do not adversely affect the performance of engineering structures. In the literature, it has been shown that  $E_{rp}$  is the potential below which stable pitting or crevice corrosion does not occur, and it is relative insensitive to prior pit depth or surface finish.

The  $E_{rp}$  can be compared to the corrosion potential ( $E_{corr}$ ) in the same environment to determine the alloy’s susceptibility to localized corrosion. If the  $E_{rp}$  is more anodic (noble) than  $E_{corr}$ , then an alloy will tend to resist pitting. If  $E_{corr}$  is more anodic, then any pits that form will tend to remain active and propagate.

An additional plot is provided in OLI Studio: Corrosion Analyzer where the corrosion potential and repassivation potential both included. The figure below shows an example for 316 stainless steel. Here the level of oxygen has been varied to show the change in corrosion potential. At low levels of oxygen, alloy 316 will have a tendency to pit readily in brackish waters.



Repassivation and Corrosion Potential for 316 stainless steel in brackish water at various levels or aeration.

### Peak Current

The peak current is defined by OLI as the current density in the most active pit. It is added as an additional line to the polarization curve. The line represents the reverse sweep in a potentiodynamic polarization experiment after pit initiation has taken place. OLI does not predict the pitting potential as it is usually a function of the history of the metal surface and is therefore variable.

Figure 20 shows the peak current for active pits superimposed on the general corrosion polarization curve.

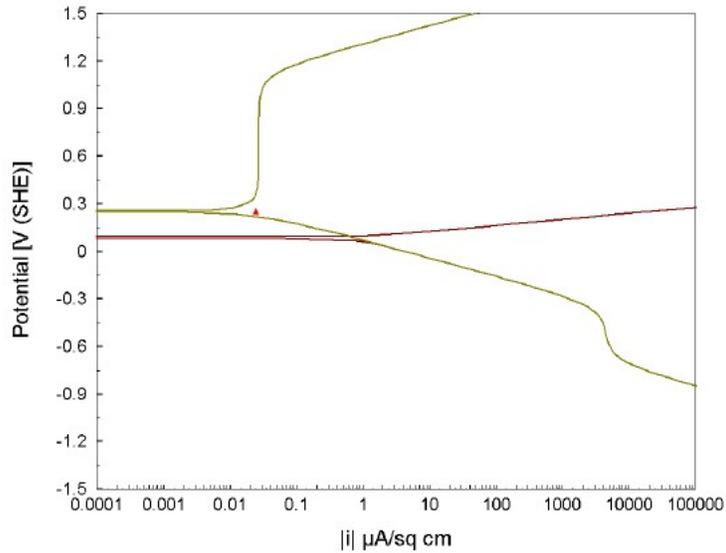


Figure 7. General corrosion polarization curve and peak current for active pits on 316 stainless in aerated sea water at 15°C under pipe flow at 2 m/s.

## Limitations

There are some phenomena that are not included in the corrosion rates code.

- Mixed solvents. The OLI Studio: Corrosion Analyzer only works in the aqueous framework. Therefore corrosion in concentrated sulfuric acid, alcohols, etc. cannot be predicted.
- Shear removal of films, often the cause of erosion-corrosion is not included in the model.
- Thin films not treated completely. The reduced transport length and gas/liquid equilibrium not entirely handled. One could still use Corrosion Analyzer to get ballpark figures for wetted surfaces.

# General Corrosion Rate and Propensity to Localized Corrosion

## Corrosion in a Sea Water Environment

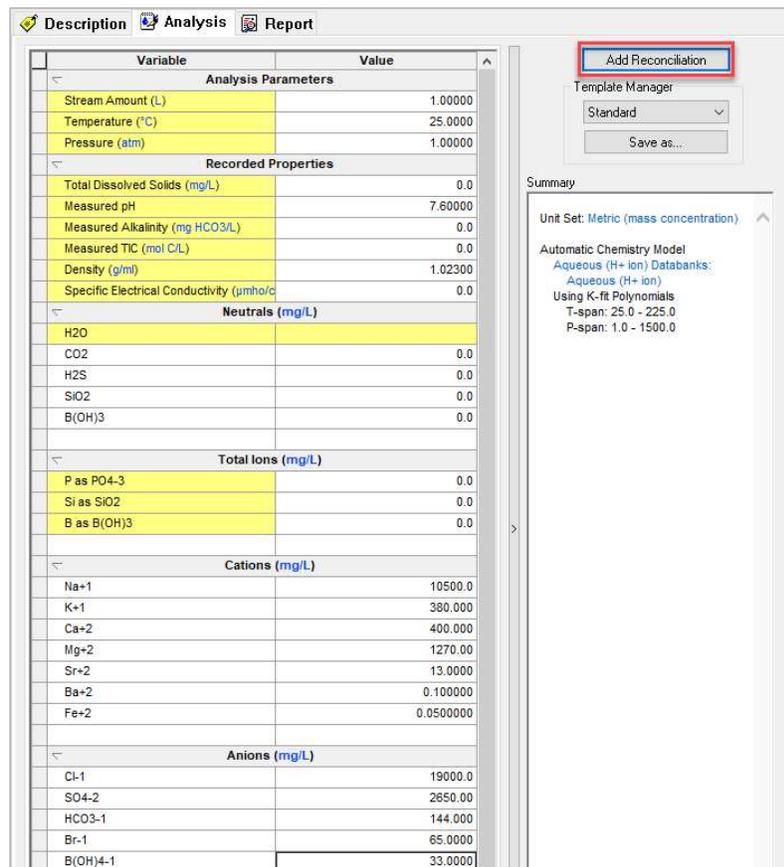
Metals used for handling sea water face both general and localized (pitting) corrosion. Various grades of stainless steels have been used to try to mitigate the problem. Stainless steels owe their corrosion resistance to a thin, adherent film of oxides on their surface. Interruption of the film can lead to localized corrosion (pitting) and premature failure. We will look at 304, 316L and S31254 (254 SMO) stainless steels and evaluate its performance in sea water as the oxygen content varies.

### Starting the Simulation

- ✓ To start the software, double-click the OLI Studio icon on the desktop  , which will take you to the OLI Studio interface where you can start creating your calculations.

For this simulation we are learning how to enter a water analysis

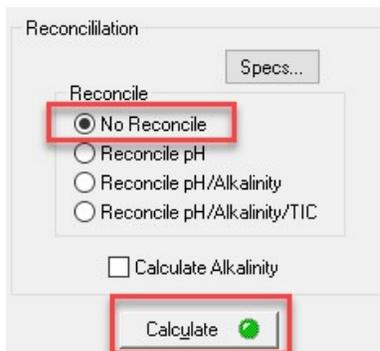
- ✓ Add a new **Water Analysis** by clicking on the **Add Water Analysis** icon  or go to the menu bar and select **Streams > Add New Analysis**
- ✓ **Click** on the new Stream and press **<F2>** to change the name to *Sea Water*
- ✓ Select the **AQ** thermodynamic Framework
- ✓ Enter the composition, temperature and pressure of the stream given in the table below



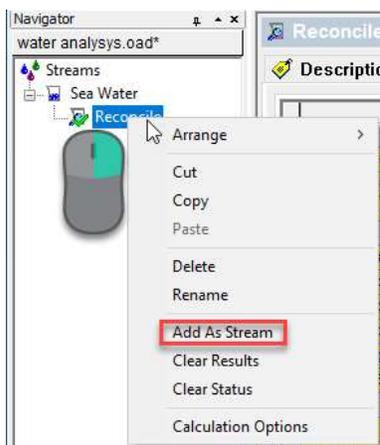
The screenshot shows the OLI Studio software interface. The main window is titled "Description Analysis Report". The "Analysis" tab is active, displaying a table of analysis parameters and recorded properties. The table is organized into several sections: Analysis Parameters, Recorded Properties, Neutrals (mg/L), Total Ions (mg/L), Cations (mg/L), and Anions (mg/L). The "Add Reconciliation" button is highlighted with a red box. The "Summary" panel on the right shows the unit set as "Metric (mass concentration)" and the automatic chemistry model as "Aqueous (H+ ion) Databanks: Aqueous (H+ ion) Using K-fit Polynomials".

Variable	Value
<b>Analysis Parameters</b>	
Stream Amount (L)	1.00000
Temperature (°C)	25.0000
Pressure (atm)	1.00000
<b>Recorded Properties</b>	
Total Dissolved Solids (mg/L)	0.0
Measured pH	7.60000
Measured Alkalinity (mg HCO <sub>3</sub> /L)	0.0
Measured TIC (mol C/L)	0.0
Density (g/ml)	1.02300
Specific Electrical Conductivity (µmho/cm)	0.0
<b>Neutrals (mg/L)</b>	
H <sub>2</sub> O	
CO <sub>2</sub>	0.0
H <sub>2</sub> S	0.0
SiO <sub>2</sub>	0.0
B(OH) <sub>3</sub>	0.0
<b>Total Ions (mg/L)</b>	
P as PO <sub>4</sub> -3	0.0
Si as SiO <sub>2</sub>	0.0
B as B(OH) <sub>3</sub>	0.0
<b>Cations (mg/L)</b>	
Na+1	10500.0
K+1	380.000
Ca+2	400.000
Mg+2	1270.00
Sr+2	13.0000
Ba+2	0.100000
Fe+2	0.0500000
<b>Anions (mg/L)</b>	
Cl-1	19000.0
SO <sub>4</sub> -2	2650.00
HCO <sub>3</sub> -1	144.000
Br-1	65.0000
B(OH) <sub>4</sub> -1	33.0000

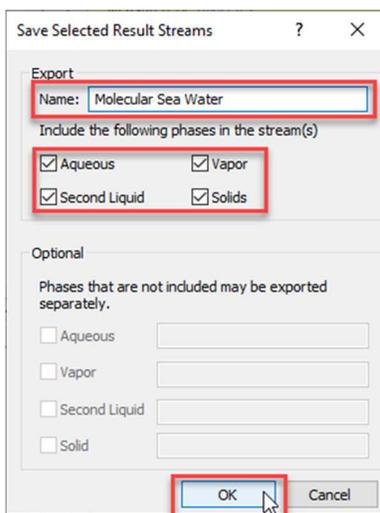
- ✓ Click on the **Add Reconciliation** button
- ✓ Select the **No reconcile** option and click on the **calculate** button



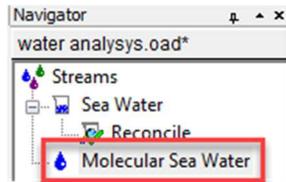
- ✓ Go to the reconciled stream  **Reconcile** and right click on it, then select **Add as Stream** option



- ✓ A new window opens. Change the name to **Molecular Sea Water**, leave the default selections and click **OK**



A new stream appears in the **Navigator Panel**



- ✓ Go to the **Add Calculation** button and select **Corrosion Rates** calculation or by selecting the **Add Corrosion Rates** icon in the Actions Pane. Your screen should look like the image below.

Variable	Value
<b>Stream Parameters</b>	
Stream Amount (L)	1.00001
Temperature (°C)	25.0000
Pressure (atm)	1.00000
<b>Calculation Parameters</b>	
Flow Type	Static
Effect of FeCO <sub>3</sub> / FeS Scales	Include
<b>Inflows (mg/L)</b>	
H <sub>2</sub> O	
B <sub>2</sub> O <sub>3</sub>	14.5699
BaCl <sub>2</sub>	0.0464401
CaCl <sub>2</sub>	1063.46
CO <sub>2</sub>	86.3342
FeCl <sub>2</sub>	0.113481
KCl	724.560
MgCl <sub>2</sub>	2254.20
MgO	1151.74
NaBr	83.7006
NaCl	26847.5
SO <sub>3</sub>	2208.57
SrCl <sub>2</sub>	23.5198
BaSO <sub>4</sub>	0.117898
CaCO <sub>3</sub>	39.8602
Fe	0.0
<b>Contact Surface</b>	
Carbon steel G10100 (generic)	

**Survey by**  
 Single Point Rate [v] Specs...  
 Then by (optional)  
 None [v] Specs...  
 Vary  
 Independently  
 Together  
 Calculate [icon]

**Summary**  
 Unit Set: Metric (mass concentration)  
 Automatic Chemistry Model  
 Aqueous (H+ ion) Databanks:  
 Corrosion (A/Q)  
 Aqueous (H+ ion)  
 Redox selected  
 Using K-fit Polynomials  
 T-span: 25.0 - 225.0  
 P-span: 1.0 - 1500.0  
 Isothermal Calculation  
 25.0000 °C 1.00000 atm  
 Calculation not done  
 Single Point  
 No secondary survey selected  
 Polarization Curve Range  
 Range -2.0 to 2.0 V (SHE)  
 Step size 0.01 V (SHE)  
 No. steps 400

- ✓ Change the default alloy **Carbon steel G10100 (generic)** to **Stainless Steel 304**
- ✓ Go to the **Survey by** option and select survey by **Composition**

Your screen should look like the image below

Variable	Value
<b>Stream Parameters</b>	
Stream Amount (L)	1.00001
Density correlation	Parent stream condition
Stream: Temperature (°C)	25.0000
Stream: Pressure (atm)	1.00000
Temperature (°C)	25.0000
Pressure (atm)	1.00000
<b>Calculation Parameters</b>	
Flow Type	Static
Thermal Aging Temperature (°C)	399.000
Thermal Aging Time (hr)	0.0
<b>Inflows (mg/L)</b>	
H2O	
B2O3	14.5699
BaCl2	0.0464401
CaCl2	1063.46
CO2	86.3342
FeCl2	0.113481
KCl	724.560
MgCl2	2254.20
MgO	1151.74
NaBr	83.7006
NaCl	26847.5
SO3	2208.57
SrCl2	23.5198
BaSO4	0.117898
CaCO3	39.8602
Fe	0.0
<b>Contact Surface</b>	
Fe(71.930)Cr(19.000)Ni(9.000)C(0.070)	

**Stainless steel 304**  
Formula = Fe(71.930)Cr(19.000)Ni(9.000)C(0.070)

Survey by: Composition Specs...

Then by (optional): None Specs...

Vary:  Independently  Together

Calculate

Summary

Unit Set: Metric (mass concentration)

Automatic Chemistry Model  
Aqueous (H+ ion) Databanks:  
Corrosion (AQ)  
Aqueous (H+ ion)  
Redox selected  
Using K-fit Polynomials  
T-span: 25.0 - 225.0  
P-span: 1.0 - 1500.0

Isothermal Calculation  
25.0000 °C 1.00000 atm  
Calculation not done

Composition survey:  
No inflow selected

No secondary survey selected

Thermal Aging Temperature: 399.000 °C  
Thermal Aging Time: 0.0 hr

Polarization Curve Range  
Range -2.0 to 2.0 V (SHE)  
Step size 0.01 V (SHE)  
No. steps 400

Metal: Stainless steel  
Stainless steel 304

Flow Type: Static  
Scales included - passivating films included.

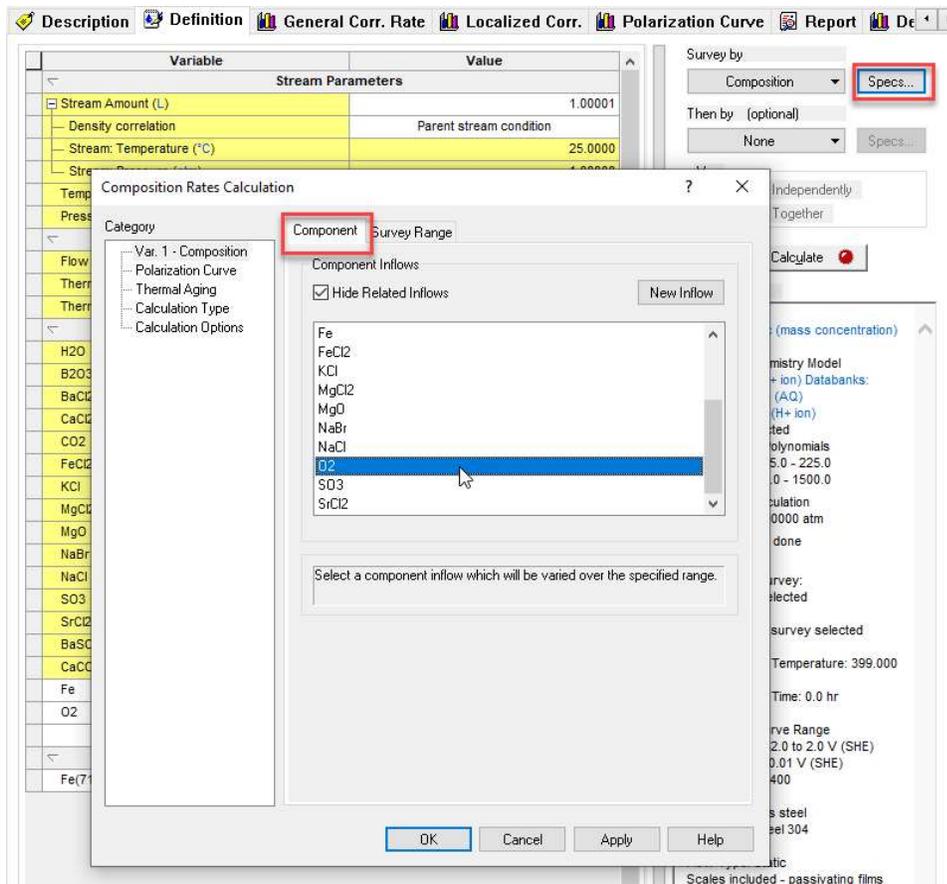
Component not selected for composition survey variable.

At this point, we need to define the variable that we are going to use for the composition survey. In this case will be oxygen.

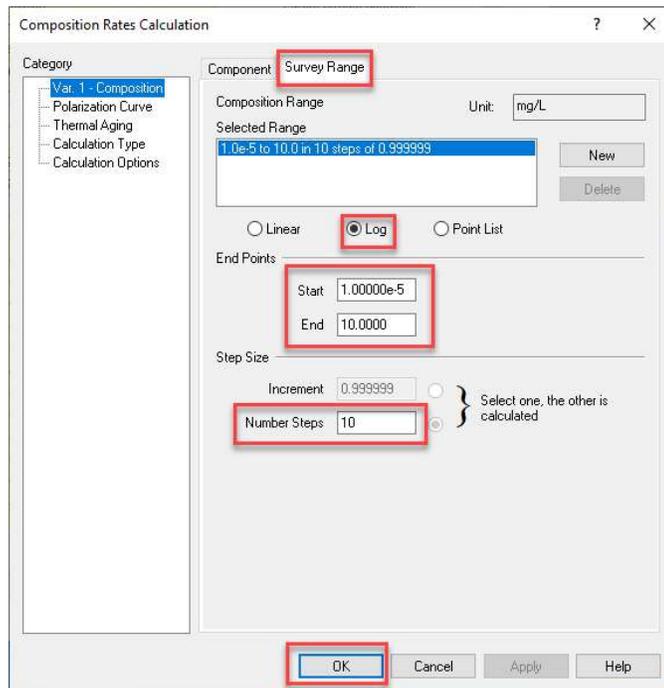
- ✓ Under **Inflows** type O2

<b>Inflows (mg/L)</b>	
H2O	
B2O3	14.5699
BaCl2	0.0464401
CaCl2	1063.46
CO2	86.3342
FeCl2	0.113481
KCl	724.560
MgCl2	2254.20
MgO	1151.74
NaBr	83.7006
NaCl	26847.5
SO3	2208.57
SrCl2	23.5198
BaSO4	0.117898
CaCO3	39.8602
Fe	0.0
O2	0.0

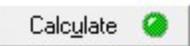
- ✓ Click on the **Specs** button (as shown in the image below). This will open a new window. **Select O2** as the component to vary



- ✓ Go to the **Survey Range** tab and enter the information given in the image below. Then click **OK**.



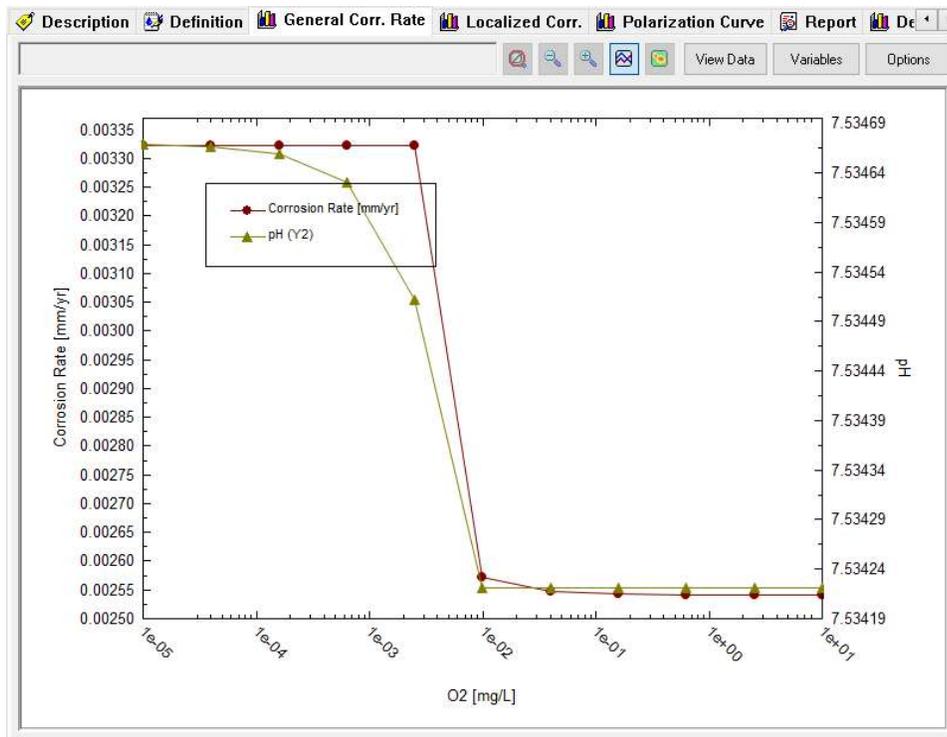
- ✓ Click the **Calculate** button



## Analyzing the Results

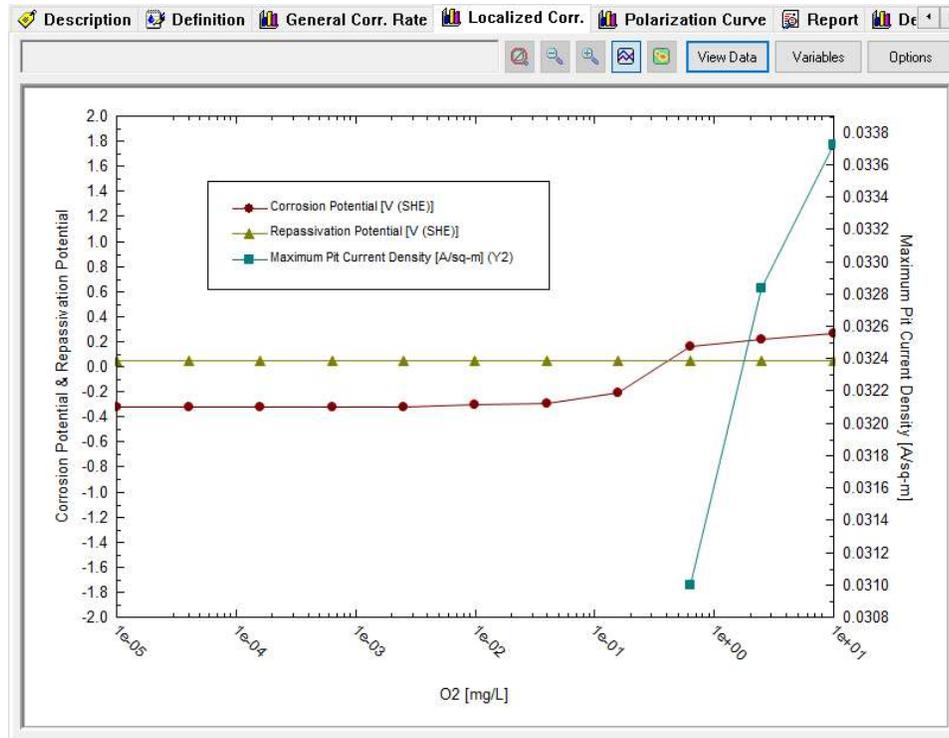
- ✓ Go to the **General Corr. Rate** tab

The default plot looks like the image below



Corrosion rate decreases as the oxygen content increases. The corrosion rate of Stainless Steel 304 is very low. From these results, one would think that SS304 would be excellent for sea water applications. At 10 mg/L of dissolved oxygen, one would predict 393.5 years of service before 1 mm of metal loss occurs. But that is not the case. Type 304 suffers greatly from localized attack in the form of pitting. Let's analyze the **Localized Corr.** tab.

- ✓ Go to the **Localized Corr.** tab

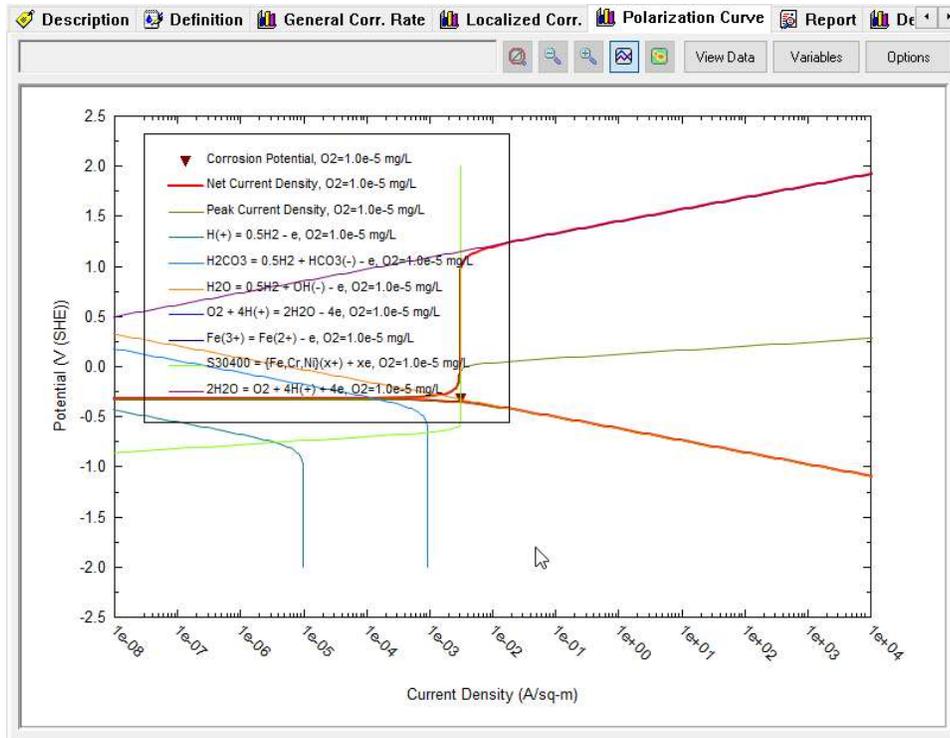


Notice that the software is predicting pitting corrosion at oxygen concentrations above 0.6 mg/L. The reason for the failure of SS304 in sea water has to do with the susceptibility of the passive film to be attacked/damaged by chlorides. The software is predicting the possible failure of type 304 by predicting the **repassivation potential** within the chemical environment it is exposed to. The repassivation potential is important because it indicates whether the metal can passivate its surface again in areas where the protective film has been damaged. When the **corrosion potential** for the surface that is undergoing general corrosion is more negative than the repassivation potential, there may be enough driving force to regrow the film; this is the case for oxygen concentrations below 0.6 mg/L, where the repassivation potential is above the corrosion potential, and localized corrosion is not predicted. Above 0.6 mg/L of oxygen concentration, SS304 suffers localized corrosion because the **dissolution rate (corrosion potential)** is higher than repassivation rate (**repassivation potential**), and hence localized corrosion is favored.

It is therefore not recommended to use type 304 for sea water applications that exceed 0.6 mg/L of oxygen content.

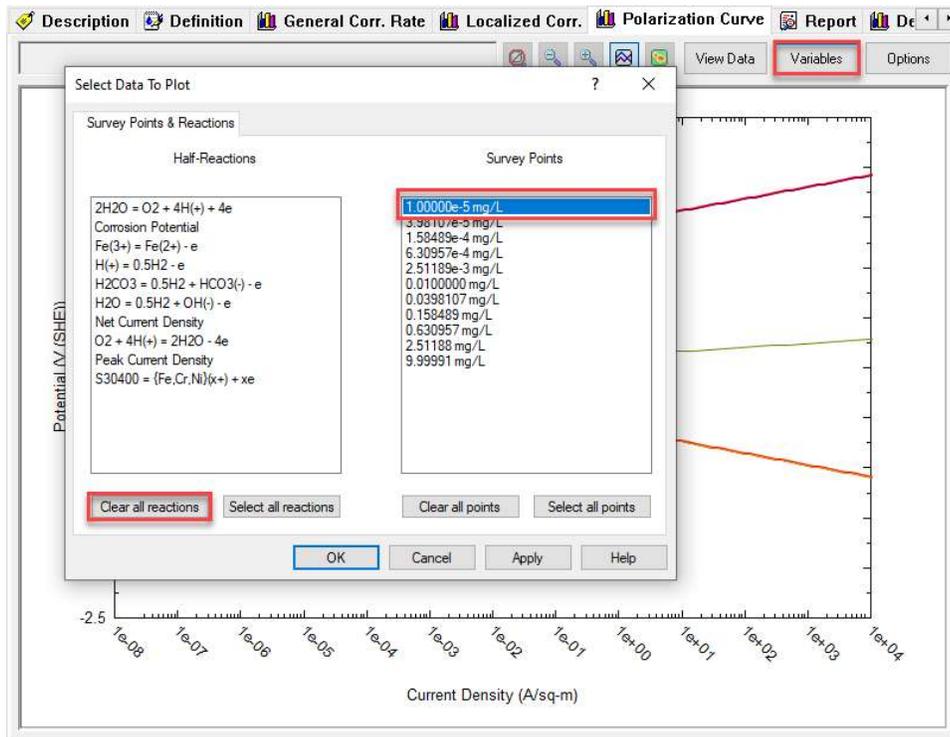
Why is the corrosion potential increases above a 0.6 mg/L of oxygen content, hence increasing the susceptibility to localized corrosion? To further understand this, we can go to the **Polarization Curve** tab.

- ✓ Go to the **Polarization Curve** tab

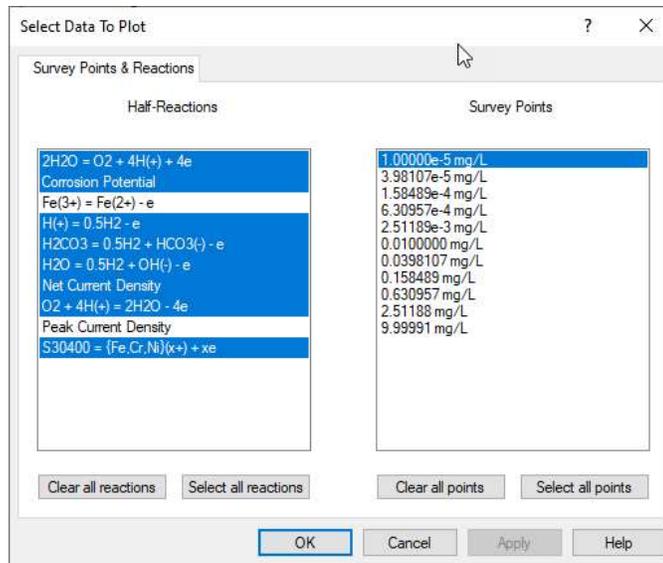


You will find a default plot shows both the net polarization curve (in red) and the half-reactions that contribute to the net polarization curve.

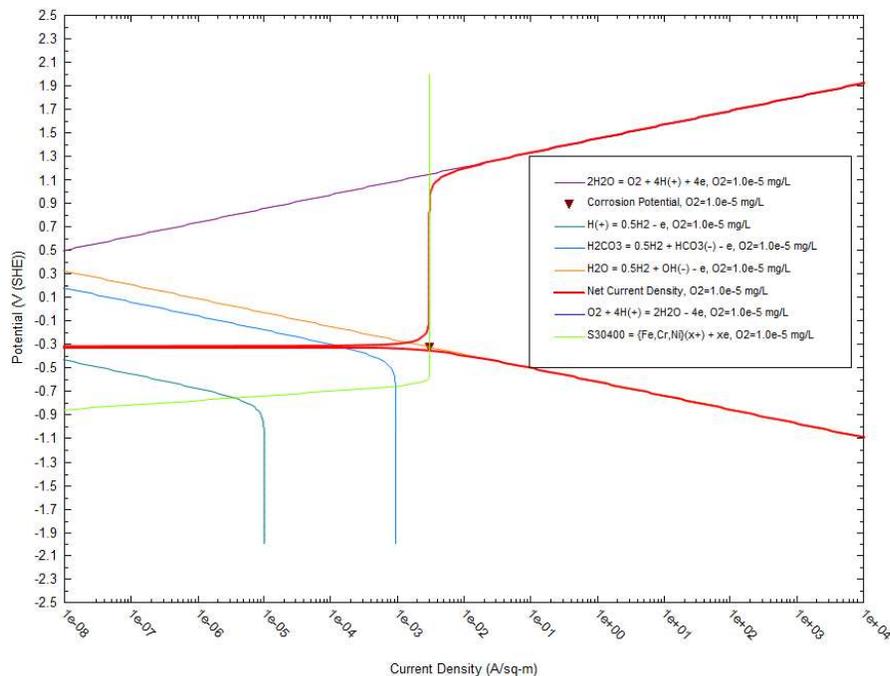
- ✓ Click on the **variables** button. This will open a new window



- ✓ Click on **Clear all reactions**
- ✓ Select the smallest concentration (1-e5 mg/L) of oxygen as shown in the image above
- ✓ Let's add the half reactions of interest. Select the reactions shown in the image below. Click OK.

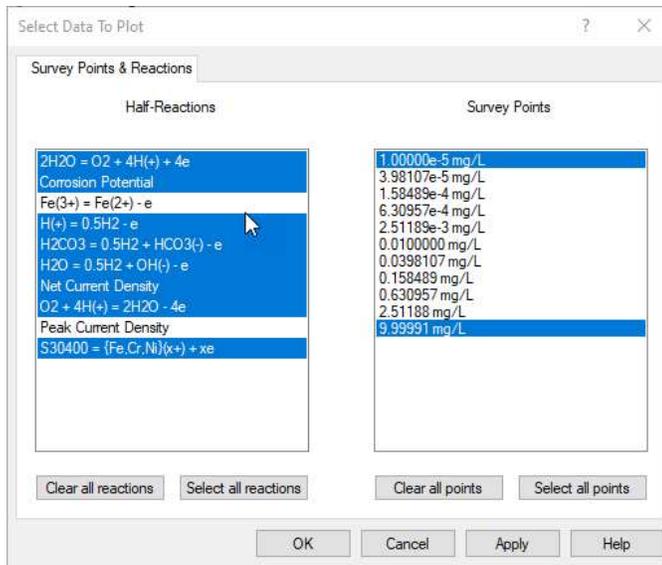


The polarization curve should look like the image below

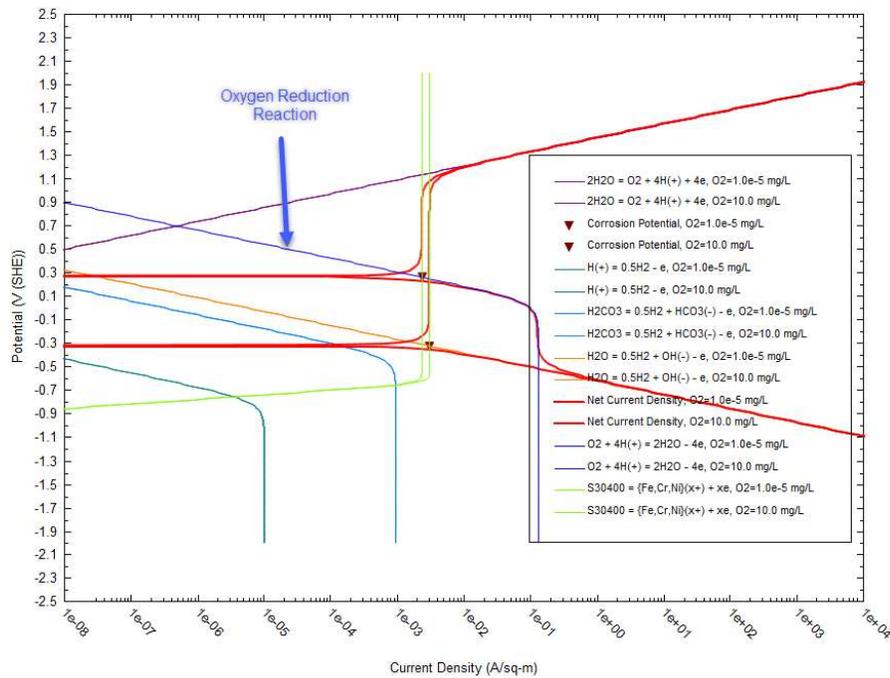


Notice that the corrosion potential (located at the red triangle) is -0.32 V vs SHE, and that the oxygen reduction reaction ( $O_2 + 4H(+) = 2H_2O - 4e$ ) is not contributing to the net current density.

- ✓ Click on the **Variables** button and add the 10 mg/L O2 curve (as shown below), and click OK



Now you will see two overlapped polarization curves.



The new polarization curve (the one located at the top of the graph) now includes the contribution to the oxygen reduction reaction (as shown by the blue arrow). The current contribution of this half-reaction changes both the total net current response and corrosion potential. The corrosion potential increased to 0.26 V vs SHE. At this 10 mg/L O<sub>2</sub> concentration, the **corrosion potential** is now higher than the **repassivation potential** (0.045 V vs SHE), hence localized corrosion is predicted.

## Bibliography

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