



## REFERENCE GUIDE TO OLI Studio: Corrosion Analyzer

think simulation

getting the  
chemistry right

## Introduction to OLI Studio

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## Disclaimer

This manual was produced using the OLI Studio: Corrosion Analyzer 11. 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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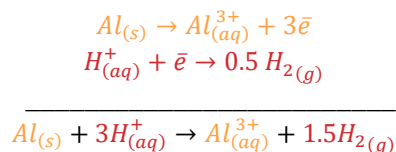
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## Chapter I – RedOx

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.

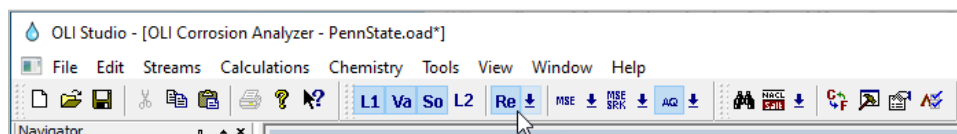
Example:



**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, purple and pink region), that are defined in the chemistry.

Periodic table of the 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	58	59	60	61	62	63	64	65	66	67	68	69	70	71				
	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu				
actinoid series	90	91	92	93	94	95	96	97	98	99	100	101	102	103				
	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr				

Alkali metals

Alkaline-earth metals

Transition metals

Other metals

Other nonmetals

Actinoid elements

Halogens

Noble gases


Rare-earth elements (21, 39, 57-71) and lanthanoid elements (57-71 only)

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

We will create an example where you will learn how to set up RedOx reactions in OLI Studio: Stream Analyzer.


### Starting the Simulation

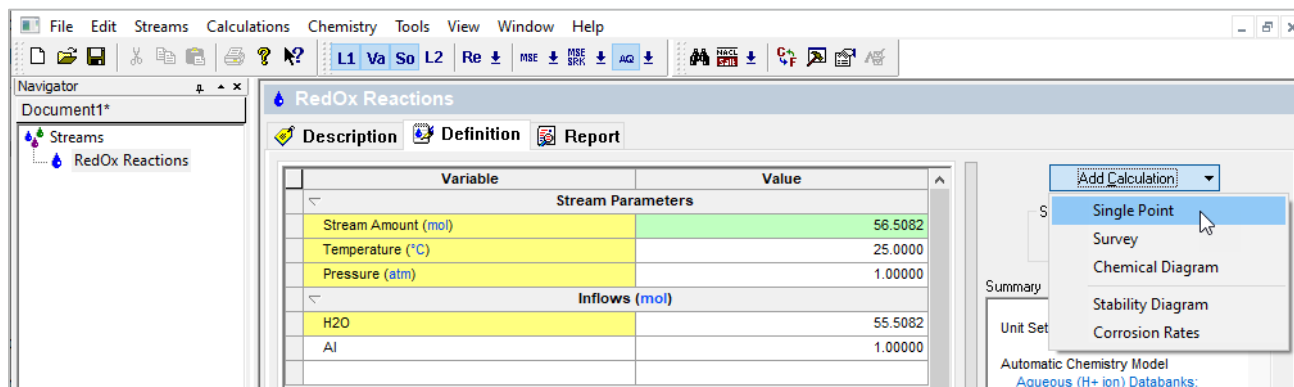
All instructions will be represented by a check mark ✓

- ✓ 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

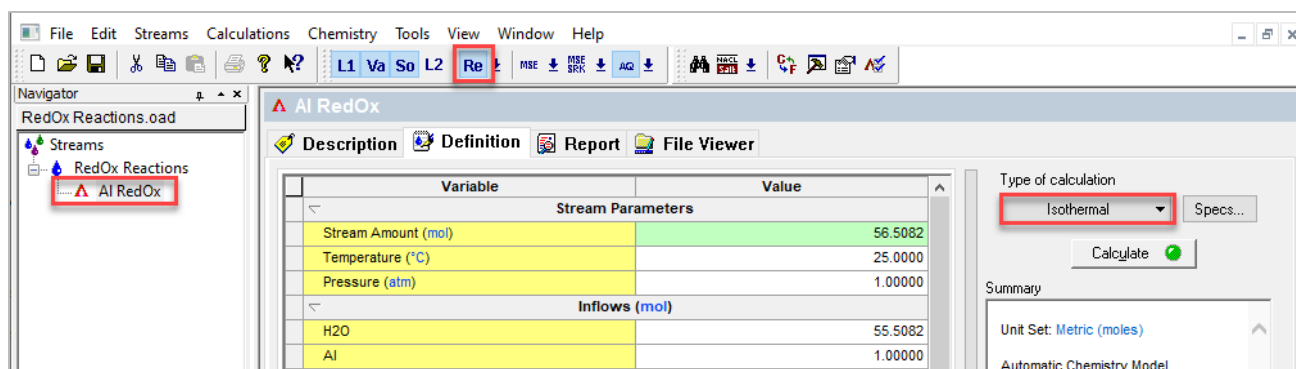


The screenshot shows the OLI Studio interface. On the left, the 'Navigator' pane shows 'Document1\*' with a 'Streams' folder containing 'RedOx Reactions'. The main window displays the 'RedOx Reactions' stream with a table of variables and values:

Variable	Value
<b>Stream Parameters</b>	
Stream Amount (mol)	56.5082
Temperature (°C)	25.0000
Pressure (atm)	1.00000
<b>Inflows (mol)</b>	
H2O	55.5082
Al	1.00000

On the right, the 'Add Calculation' menu is open, showing options: Single Point, Survey, Chemical Diagram, Stability Diagram, and Corrosion Rates. The 'Single Point' option is highlighted. Below the menu, it says 'Automatic Chemistry Model Aqueous (H+ ion) Databanks:'.

- ✓ 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



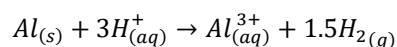
- ✓ Click on the **calculate** button -
- ✓ Click on the **Report** tab and scroll down to the **Element Balance** table

Jump to: Element Balance

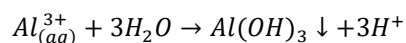
Row Filter Applied: Only Non Zero Values  
column Filter Applied: Only Non Zero Values

	Total mol	Aqueous mol	Vapor mol	Solid 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.





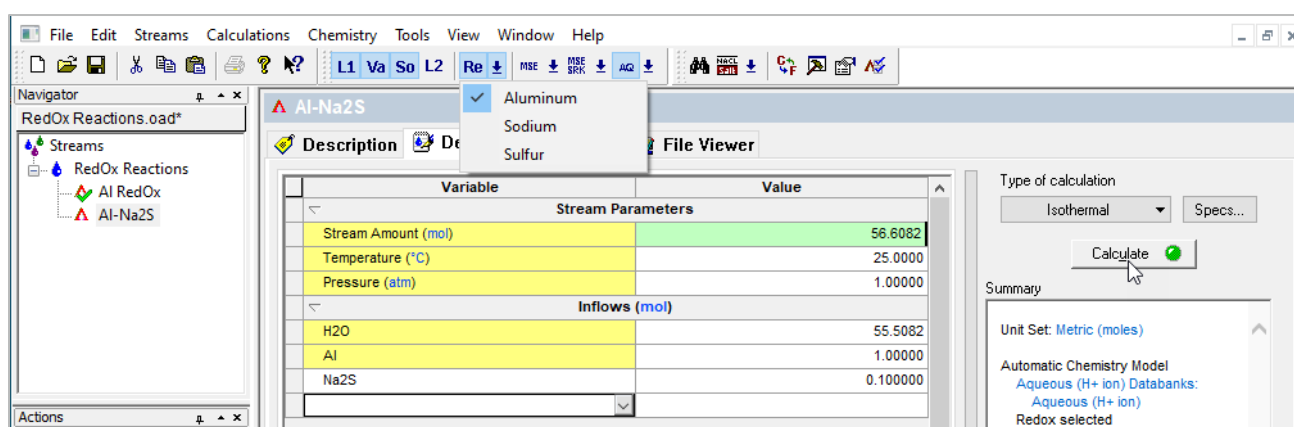
## No Transition Metals

In this example,  $\text{Na}_2\text{S}$  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  $\text{Na}_2\text{S}$  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



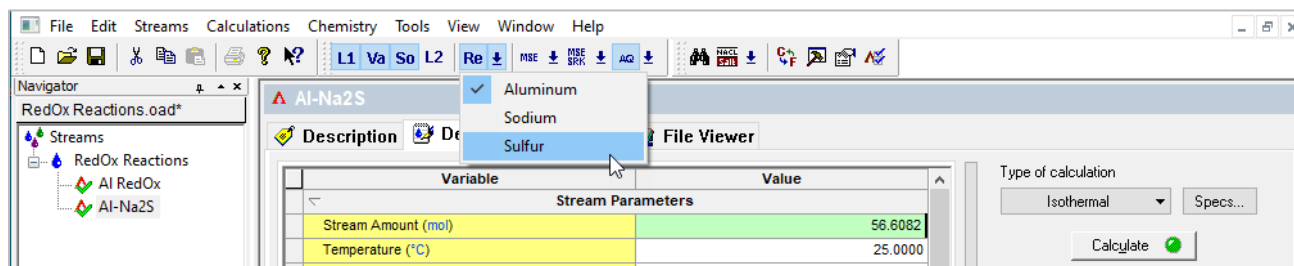
- ✓ Click on the **Report** tab and scroll down to the **Element Balance** table

The screenshot shows the 'Element Balance' table. The 'Report' tab is active, and the 'Element Balance' table is displayed. The table shows the balance for various elements across different phases (Total, Aqueous, Vapor, Solid).

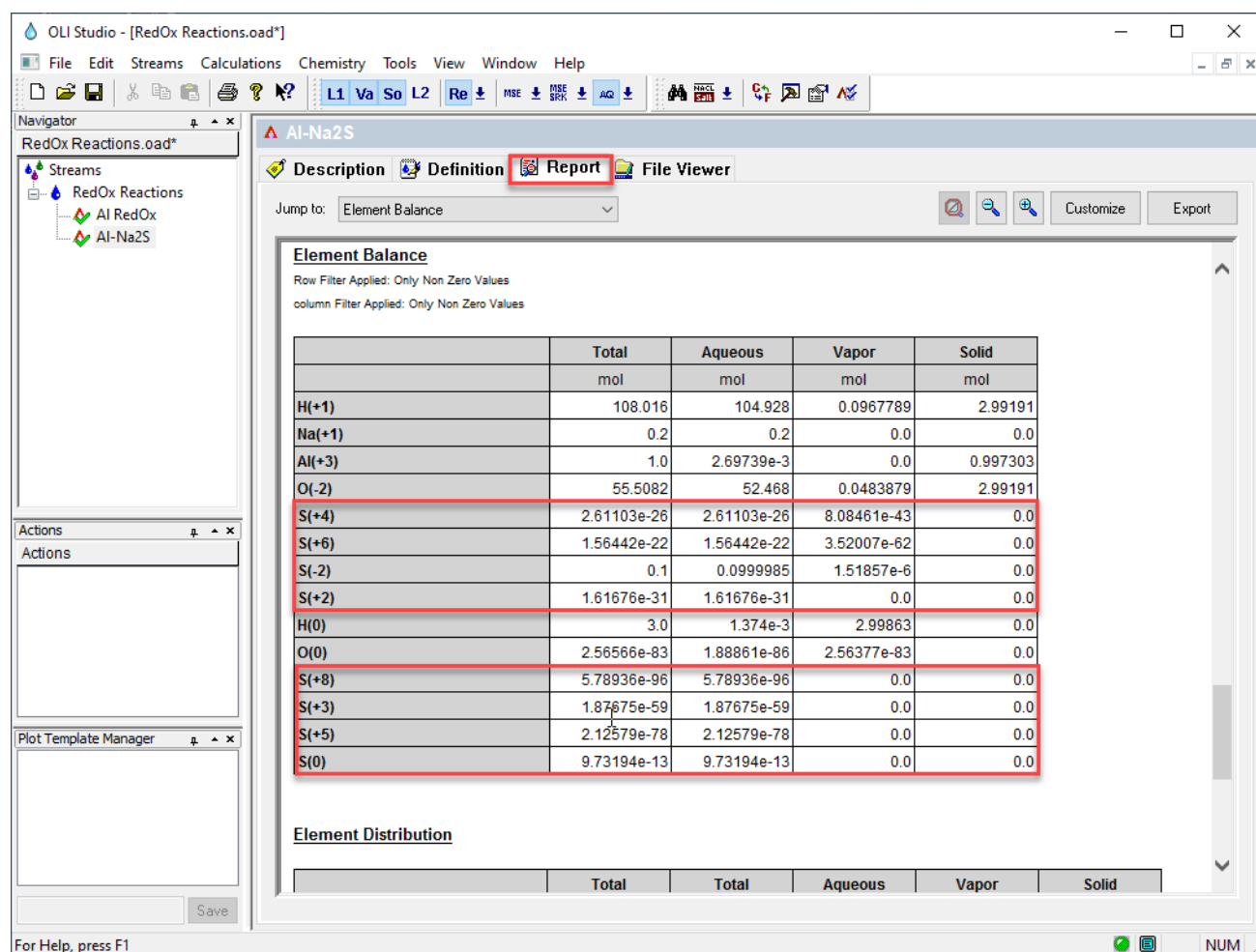
	Total	Aqueous	Vapor	Solid
	mol	mol	mol	mol
H(+1)	108.016	104.928	0.0967789	2.99191
Na(+1)	0.2	0.2	0.0	0.0
Al(+3)	1.0	2.69739e-3	0.0	0.997303
O(-2)	55.5082	52.468	0.0483879	2.99191
S(-2)	0.1	0.0999985	1.51857e-6	0.0
H(0)	3.0	1.374e-3	2.99863	0.0
O(0)	2.56566e-83	1.88861e-86	2.56377e-83	0.0

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?

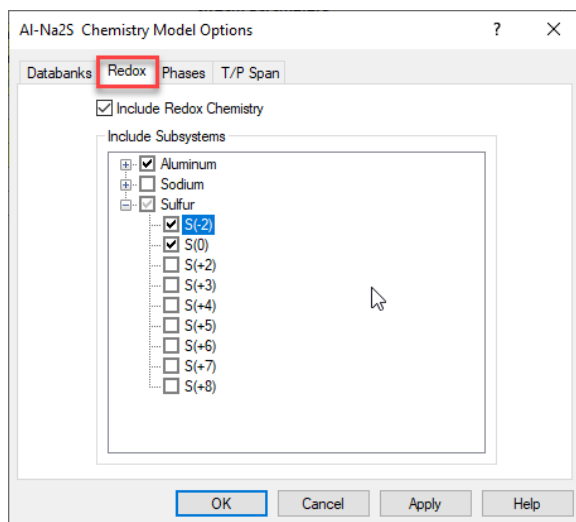
## Selecting Specific Oxidation States

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...**

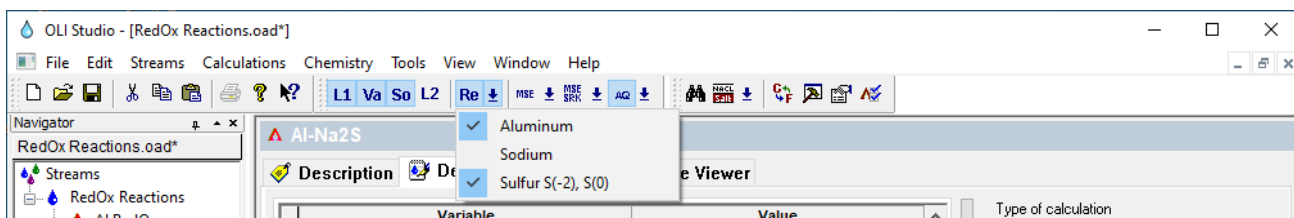


- ✓ A new window opens. Select the **Redox** tab and expand the **Sulfur** subsystem. In here you can enable and disable all or specific oxidation states. Let's say we want to include the following oxidation states: -2 and 0 only, so the window will look like the image below.
- ✓ Click **OK**



- ✓ 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

OLI Studio - [RedOx Reactions.oad\*]

File Edit Streams Calculations Chemistry Tools View Window Help

Navigation: RedOx Reactions.oad\*

Streams: RedOx Reactions, Al RedOx, Al-Na2S

Actions: Actions

Al-Na2S

Description Definition **Report** File Viewer

Jump to: Element Balance

Row Filter Applied: Only Non Zero Values  
column Filter Applied: 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.

## Chapter II – Pourbaix Diagrams

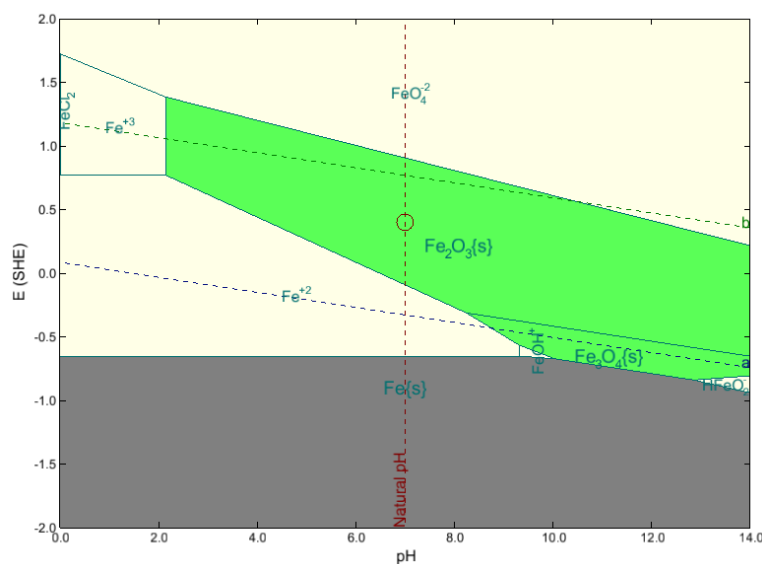
A Stability Diagram also known as Pourbaix Diagram or simply Potential vs pH diagram, maps out the possible stable species in an aqueous environment at different pH and potential combinations. This diagram, however, does not provide information of reaction rates or kinetic effects.

### Interpretation of the Stability Diagram

Stability (Pourbaix) diagrams are a form of predominance diagrams created with two independent variables. They are pH on the x-axis and standard reduction potential in the y-axis. A schematic representation of the Pourbaix diagram for Iron in water at 25 °C and 1 atm is shown in the image below.

The basic features of a stability diagram are:

- The dominant species is presented at any given point and not all species that would occur.
- The bottom of the diagram refers to reduced species, i.e., Fe(s), or to the type of conditions that lead to reduction.
- The top of the diagram refers to oxidized species and/or oxidizing conditions.
- Vertical lines indicate changes in acid/base chemistry independent of potential (E), e.g., Fe<sup>3+</sup> to Fe(OH)<sub>3</sub>.
- Horizontal lines indicate redox changes unaffected by pH, e.g., Fe to Fe<sup>2+</sup> below pH 6.
- The sloped lines indicate that both potential (E) and pH changes (i.e. [H<sup>+</sup>] or [OH<sup>-</sup>]) affect the redox process.



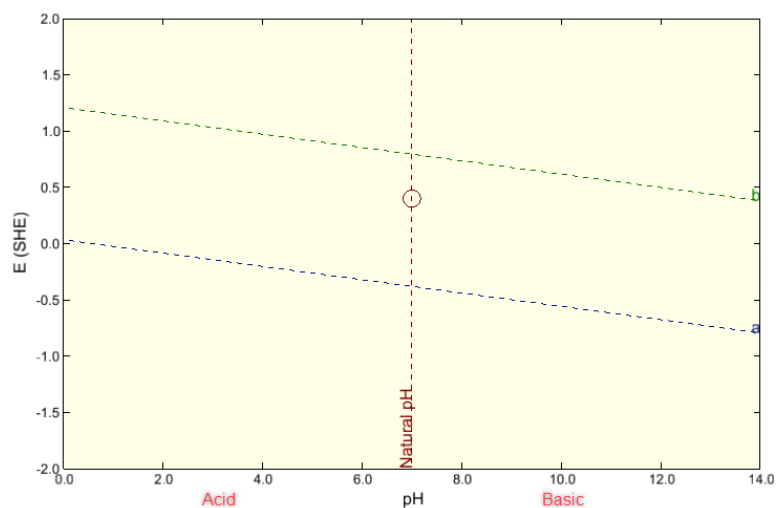
Pourbaix Diagram of Iron in Water

The stability diagrams contain a great deal of information, so it is important to describe in more detailed the information that is being presented, and these are: Water stability region, ORP, Natural pH, Passivity region, Immunity region and the Corrosion region.

## 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.

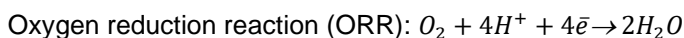
The diagonal dashed lines, represented by the letters **a** and **b** are the water reduction and water oxidation lines, respectively.



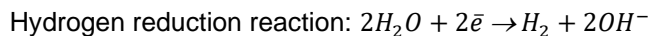
Stability field of water

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.

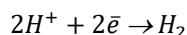
In an **acid** solution, the primary redox reactions are:



In a **basic** solution, the primary redox reactions are:



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



Equation 1

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  $H_2$  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**. The  $H^+/H_2$  half-cell reaction is at thermodynamic equilibrium along this line, which has a slope equal to -0.059 at room temperature. Above this line, water ( $H^+$ ) is the stable phase and  $H_2(sol.)$  is oxidized. Below this line,  $H_{2(g)}$  is the stable phase and water ( $H^+$ ) is reduced.

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



And the potential (E) is given by:

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

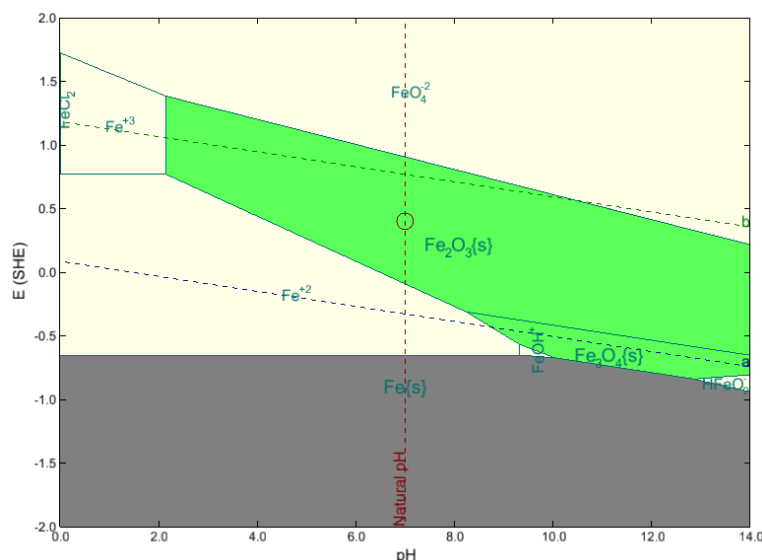
Equation 4 is shown in the above figure as the green dashed line, label **b**. Above the oxygen line,  $O_{2(g)}$  is the stable phase, and water (or  $OH^-$ ) is oxidized. Below the oxygen line, water is stable, and  $O_{2(sol.)}$  is reduced.

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, dashed 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  $Fe_2O_3$  and  $Fe_3O_4$  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,  $Fe^{2+}$  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 diagram shows oxides are 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 (Bulk solution)
- Selecting the right titrants
- Selecting the metallic surface, i.e., metal, element, alloy, etc.
- Formatting – Optional

### Environment Creation (Bulk Solution)

The chemical environment (bulk solution) in which a particular metal will corrode needs to be entered before the stability analysis can be calculated, even is 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.

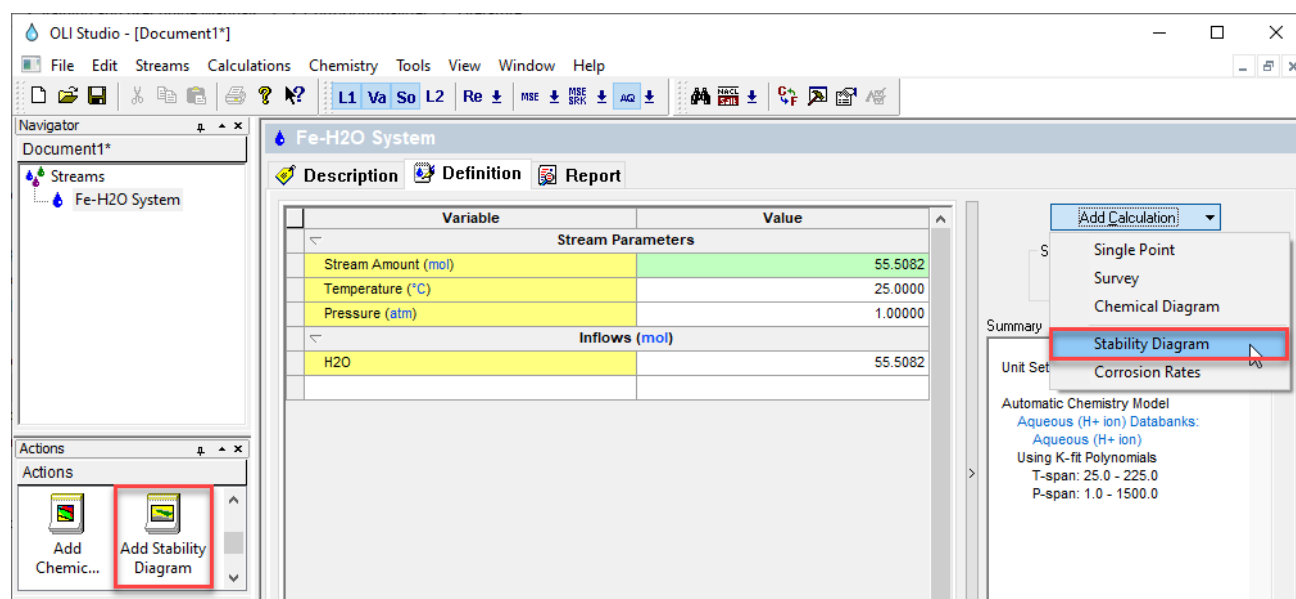
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<sup>1</sup> Pourbaix, M.1966. Atlas of electrochemical equilibria in aqueous solutions. Houston, Tex.: National Association of Corrosion Engineers

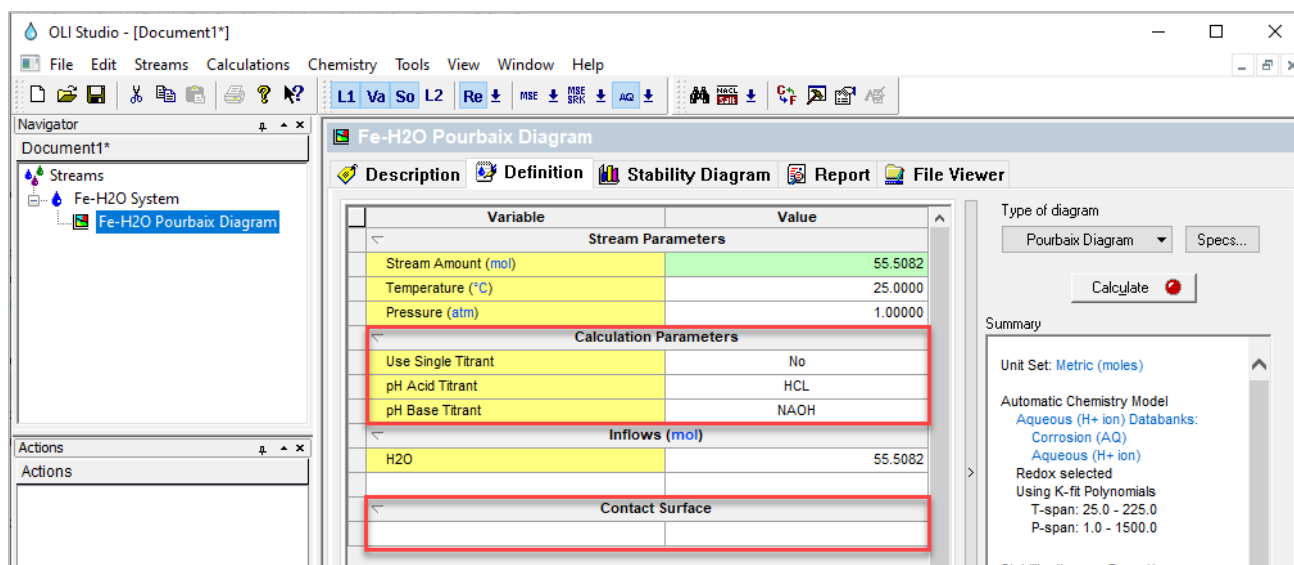
For this example, we are going to use the **Add Stream** option. Use the inputs and parameters from the table below to create the stream's composition. Certain inputs, such as the name style, units, etc. will require further adjustments, and will be described as necessary.

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

- ✓ 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.

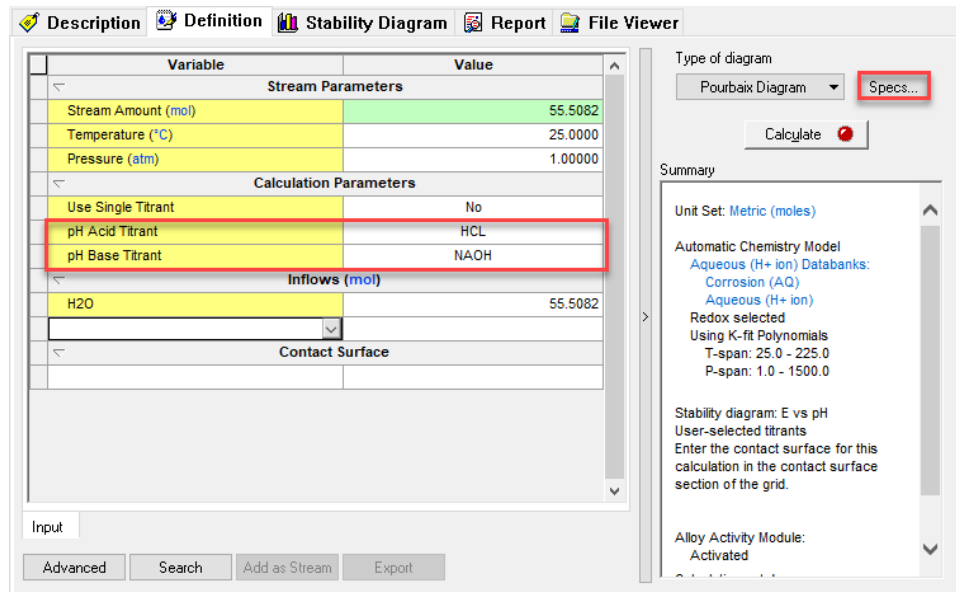
In the **Contact Surface** grid is where the metal or alloy of interest needs to be defined. E.g. Fe, Cu, carbon steel, etc.

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.



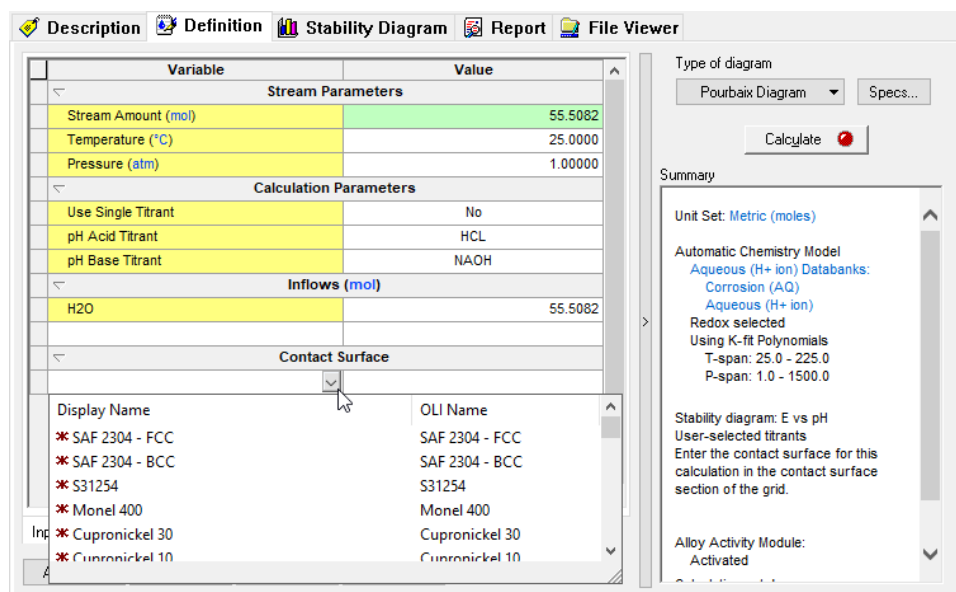
Default titrants HCl and NaOH are added to the defined chemistry to move along the x-axis of the stability diagram.  
The default titrants can be change by clicking on the Specs...button.

- ✓ 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.

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	
Mo	
Cr	

Summary

Unit Set: Metric (moles)

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

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

Chromium

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>

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 (AQ)

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

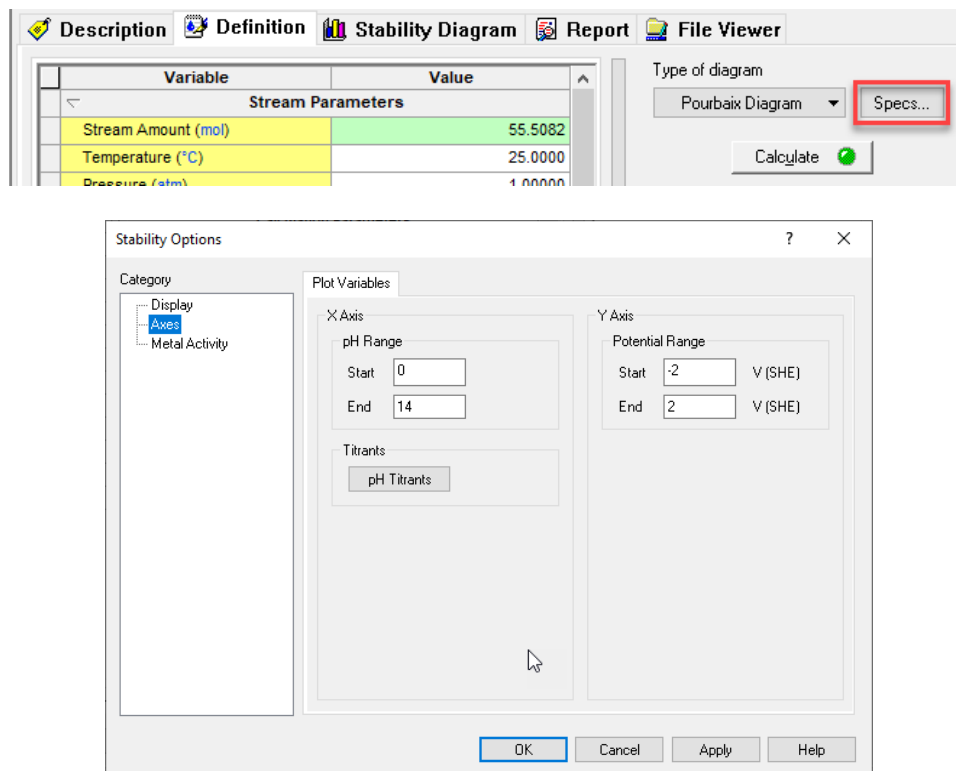
Iron

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.



## 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, if 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.

$$e = e^0 - \frac{RT}{2F} \ln \frac{a_{Fe}}{m_{Fe^{2+}} \gamma_{Fe^{2+}}}$$

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.

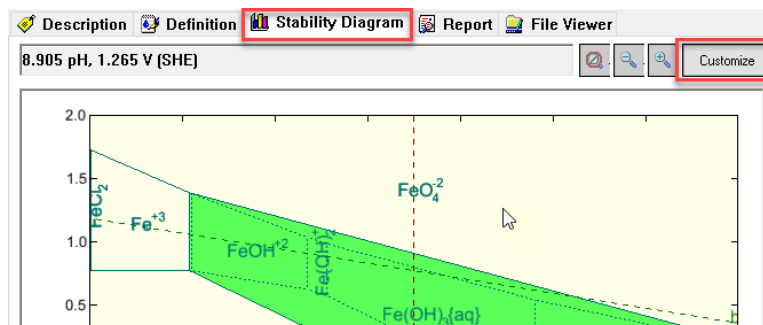
You can change the trace default value in the **Definition** tab, by clicking on the **Specs...** button and then select **Metal Activity**.



## 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.

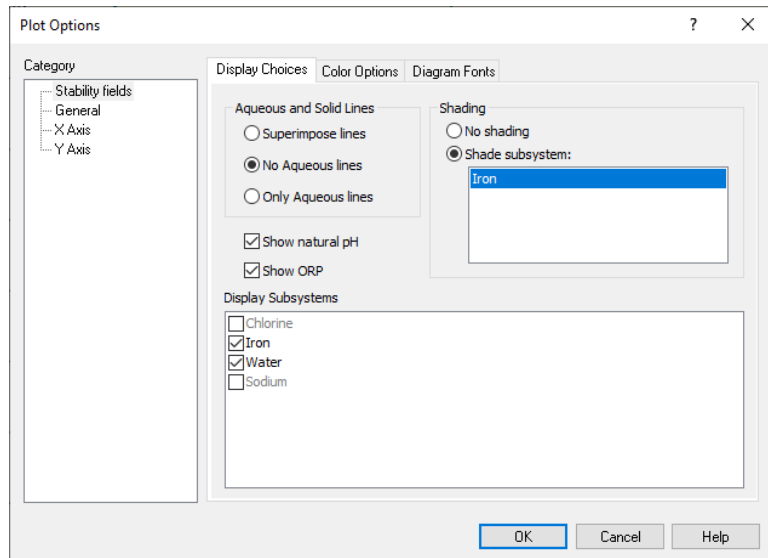


This opens a new window. Under the **Display Choices** tab, you can find the following sections:

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 dashed 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



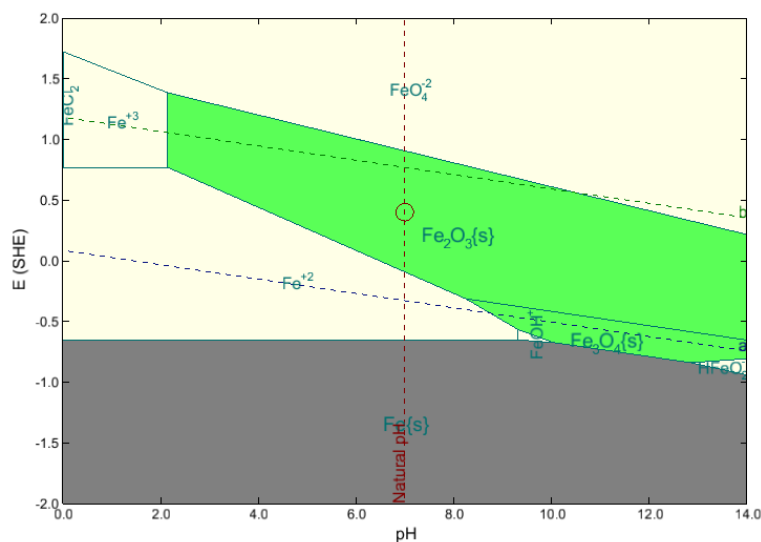
- ✓ Click **OK**



- ✓ 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  $\text{Fe}_3\text{O}_4$  (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  $\text{Fe}_2\text{O}_3$  (hematite). Hematite is the dehydrated form of  $\text{Fe}(\text{OH})_3$  and  $\text{FeOOH}$ , 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  $\text{Fe}^{+2}$ . 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  $\text{Fe}_2\text{O}_3$  (hematite) is the most stable species that forms.

Additionally, notice that the oxidation of iron can be coupled with the hydrogen reduction reaction because the  $\text{H}^+$  reduction line (line a) lies above the equilibrium 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.,  $\text{Fe}^{2+}$ .

## Modeling the Effects of Hydrogen Sulfide on Corrosion

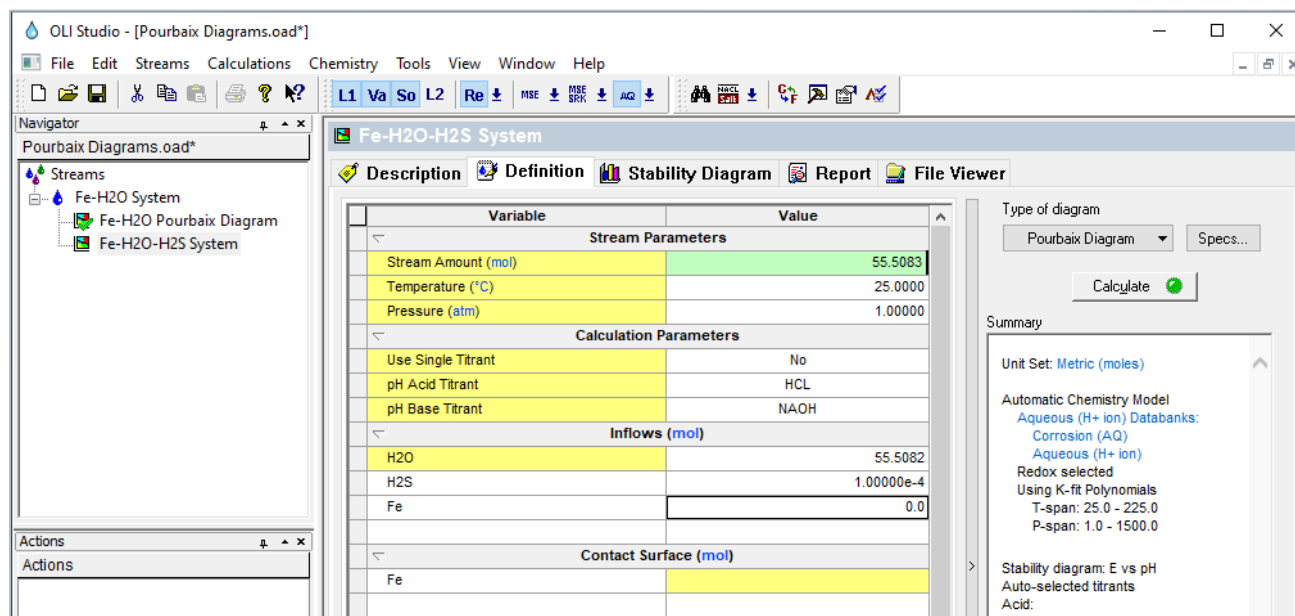
The  $\text{H}_2\text{S}$  ( $\text{S}^{2-}$ ) forms a relatively insoluble precipitate with  $\text{Fe}^{+2}$ . This precipitate has the potential to cover the metal surface and enhance the pH region where iron is protected from the water. We will model this using the Stability Diagram tool.

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

OLI Studio - [Pourbaix Diagrams.oad\*]

File Edit Streams Calculations Chemistry Tools View Window Help

L1 Va So L2 Re MSE MSE SRK AQ

Navigator

Pourbaix Diagrams.oad\*

Streams

- Fe-H2O System
  - Fe-H2O Pourbaix Diagram
  - Fe-H2O-H2S System

Actions

Fe-H2O-H2S

Iron

Sulfur

Description

Variable	Value
<b>Stream Parameters</b>	
Stream Amount (mol)	55.5083
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
H2S	1.00000e-4
Fe	0.0
<b>Contact Surface (mol)</b>	
Fe	

Stability Diagram

Report

File Viewer

Type of diagram

Pourbaix Diagram

Specs...

Calculate

Summary

Unit Set: Metric (moles)

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

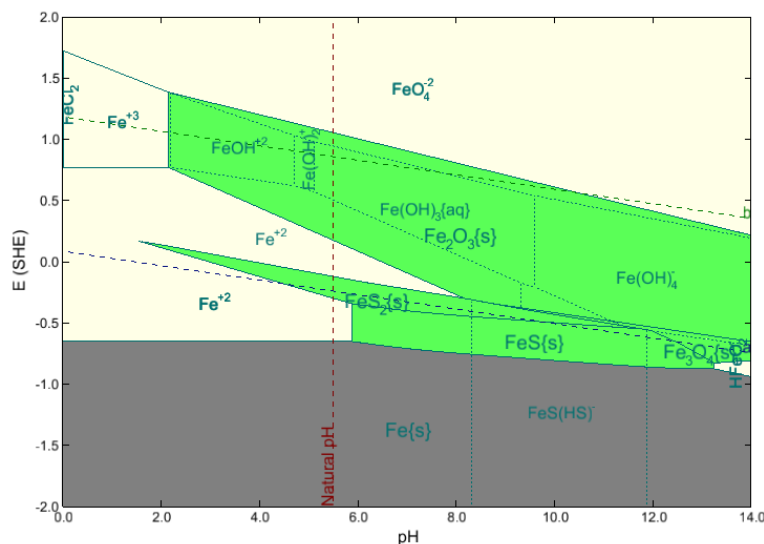
Stability diagram: E vs pH


Auto-selected titrants

Acid:

- ✓ 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. 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 (Theory)

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.

### Equilibrium Potential, $E^{eq}$

The equilibrium potential (or reversible potential) describes the equilibrium between two different oxidation states of the same element, at whatever concentration (or pressure) they occur. The reaction moves away from equilibrium only if there is a source or sink for electrons.



### Standard Equilibrium Potential, $E^0$

$E^0$  is the equilibrium potential for the same reaction  $Me \leftrightarrow Me^{n+} + z\bar{e}$  defined at standard conditions.

### Nernst Equation

The equilibrium potential  $E^{eq}$  varies with concentration, pressure, and temperature. There is an equation that links the equilibrium potential of an electrode,  $E^{eq}$ , to its standard potential,  $E^0$ , and the concentrations of the reacting components at a given temperature and pressure, and that is the **Nernst equation**.

For the reaction:



The Nernst Equation\* can be written as:

$$E^{eq} = E^0 - \frac{RT}{zF} \ln \left( \frac{\prod (a_{reduced})^j}{\prod (a_{oxidized})^k} \right)$$

Or

$$E^{eq} = E^0 - \frac{RT}{zF} \ln \frac{a_{Me^{n+}}}{a_{Me}}$$

The Nernst equation is an extremely rich tool for a first approach of the analysis and comprehension of corrosion processes.

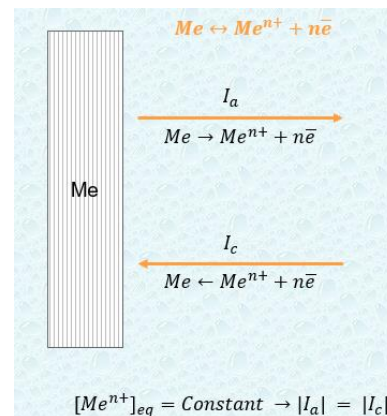
## Kinetics at Equilibrium

### Exchange Current Density

Let's imagine that we immersed a sample in solution, containing a certain number of cations in solution. The following forward-backward redox reaction at equilibrium occurs:  $Me \leftrightarrow Me^{n+} + n\bar{e}$

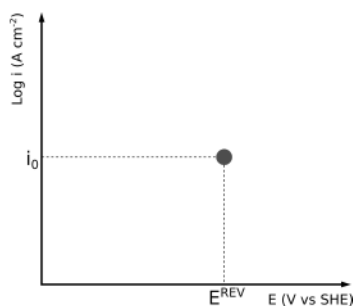
At any given interval of time the same number of moles of metal and number of electrons ( $n$ ) is produced by the metal dissolution, corresponding to an anodic current  $I_a$ , and at the same time they are consumed by the metal deposition on the metallic surface, corresponding to a cathodic current,  $I_c$ .

A dynamic equilibrium condition exists at the surface where the rate in the forward direction (i.e., the oxidation or anodic reaction),  $r_f$ , **equals** the rate in the reverse direction (i.e., reduction or cathodic reaction),  $r_r$ .



Dissolution and deposition are the forward and backward elementary steps of the overall reaction, and take place at the same rate, thus yielding  $I_a + I_c = 0$  or  $|I_a| = |I_c| = I_o$ , where  $I_o$  is the exchange current

When the reaction is at equilibrium, the electrode potential is equal to the equilibrium potential,  $E^{eq}$  a.k.a. reversible potential,  $E^{rev}$  and the corresponding current is the exchange current density,  $i_o$ .



## Kinetics away from Equilibrium

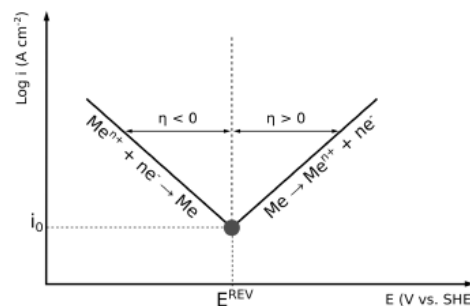
### Overpotential, $\eta$

So far, we have studied reactions at equilibrium, for which zero overall current characterizes the electrochemical system. In corrosion we are seldom at conditions near thermodynamic equilibrium, in fact, most reactions occur far from  $E^{eq}$ . Thus,

If  $E > E^{eq} \rightarrow$  half-cell reaction will go in the oxidizing (i.e., anodic) direction

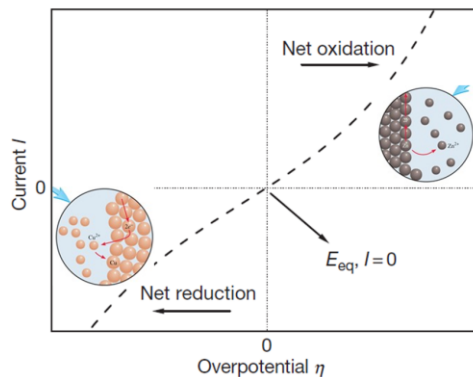
If  $E < E^{eq} \rightarrow$  half-cell reaction will go in the reducing (i.e., cathodic) direction.

Polarization,  $\eta$ , is a change in potential from the equilibrium half-cell potential, i.e.,  $\eta = E - E^{eq}$ .  $\eta$  is also known as **overpotential**.



The relationship between current and overpotential describes the kinetics of the system, and it can be plotted in the form of current vs overpotential, as shown in the plot below.

This is another way to represent the current-overpotential curve involving the anodic and cathodic reactions:

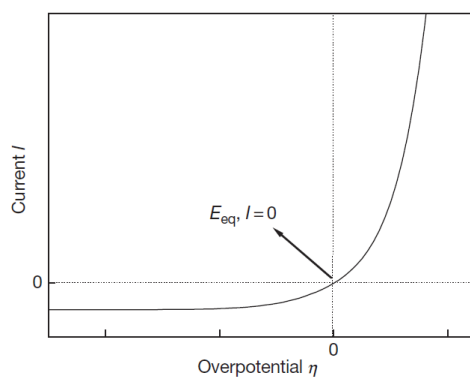


Schematic drawing of the current-overpotential involving the cathodic (net reduction) and the anodic (net oxidation) domains

The plot above is called a polarization curve. In this plot the product  $I\eta$  is always positive, the higher the overpotential the higher the net current.

For the product  $I\eta$  to always increase it requires two conditions

1. In the anodic region, the metal is always available at the interface so that, whatever the overpotential, the metal can keep supplying cations.
2. In the cathodic region, the cations must be available to ensure the increase in current ( $I$ ) with increasing overpotential. However, beyond a certain overpotential, the amount of cations arriving at the interface per unit time is limited by mass transport. The consequence is that the current reaches a diffusion limiting plateau as shown in the figure below.



Schematic representation of a current-overpotential curve with mass transport-controlled plateau in the cathodic domain

The plot above shows that the actual current flow is the result of combined kinetic phenomena, charge transfer of the reactions and mass transport of the cations.



We are going to learn in more detail when the kinetics are controlled by a single phenomenon and the general case of mixed control.

## Activation Polarization

In this case the interfacial kinetics are the controlling factor. The influence of mass transport here is negligible, in particular diffusion, because it is much faster than the charge-transfer process.

Therefore, the concentrations are identical at the interface and in the electrolyte bulk:

$$[Ox]_{int} \approx [Ox]_{\infty} \text{ and } [Red]_{int} \approx [Red]_{\infty}$$

When the **concentration** of the reactants and products at the electrode surface are the same as in the bulk solution, the overpotential resulting from a potential change is called **activation overpotential** or charge-transfer overpotential.

If there is a **change** in the **electrode potential** this will **change** the **rate of the electrochemical reactions** occurring on the surface by altering the rate of charge transfer.

The equation that fully describes the kinetic behavior of an electrochemical interface in the case of pure activation control is the **Butler-Volmer Equation**. This equation shows the relationship between the rate of reaction (current density,  $i$ ) and the driving force,  $E$ .

$$i = i_o \left( \exp\left(\frac{\alpha z F}{RT} \eta\right) - \exp\left(-\frac{(1-\alpha) z F}{RT} \eta\right) \right)$$

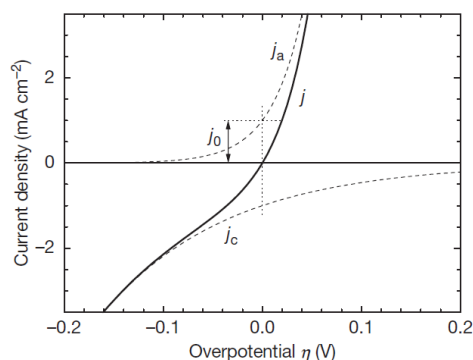
Anodic Current      Cathodic Current

Where:

$i$  is the total current density  
 $i_o$  is the exchange current density  
 $\alpha$  symmetry factor (usually 0.5 but between 0 and 1)  
 $\eta = E - E^{eq}$  is the overpotential

By definition, an anodic current is taken as positive, while a cathodic current is taken negative.

The two terms in the right-hand side of the **Butler-Volmer** equation stand for the purely anodic and cathodic branches of the current-overpotential curve. These are represented by the dashed lines on the plot below.



Current-overpotential curve of a purely charge-transfer controlled system illustrating  $j_a$  and  $j_c$  in the upper and lower halves, respectively (dashed lines) and the overall Butler-Volmer equation (solid line):  $\alpha=0.5$ ,  $z=1$  and  $j_0=1\text{mA/cm}^2$

The net current is the addition of the two currents at each overpotential, and it is represented by the solid line. It represents the net current of the anodic and cathodic contributions.

At equilibrium we have the zero current represented by the exchange current density.

Finally, the charge transfer coefficient or symmetry factor, indicates how the electrical energy supplied to the electrochemical system is shared between the anodic and cathodic reactions. The value  $\alpha=0.5$  indicates that both reactions are boosted or slowed down by the same factor.

## Tafel Behavior – High Overpotential Limiting Case

When a large overpotential is applied to the interface, one of the exponential terms of the Butler-Volmer equation vanishes and the corresponding reaction can be neglected.

For example, for the anodic case, if a sufficiently large anodic overpotential is applied, the contribution to the net current from the cathodic current can be neglected.

Thus, for positively charged overpotential

$$i \approx i_a = i_o \exp\left(\frac{\alpha z F}{RT} \eta\right)$$

For negatively charged overpotential

$$i \approx i_c = -i_o \exp\left(-\frac{(1-\alpha) z F}{RT} \eta\right)$$

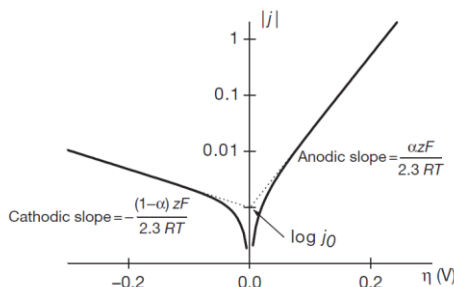
After some mathematical treatment the equations can be represented in a logarithmic form:

$$\log i \approx \log i_a = \log i_o + \frac{\alpha z F}{2.3 RT} \eta \quad \text{anodic current}$$

$$\log(-i) \approx -\log(i_c) = \log i_o - \frac{(1-\alpha) z F}{2.3 RT} \eta \quad \text{cathodic current}$$

The terms  $\frac{\alpha z F}{2.3 RT} \eta$  and  $\frac{(1-\alpha) z F}{2.3 RT} \eta$  are known as the anodic and cathodic Tafel coefficients,  $\beta_a$  and  $\beta_c$

In a plot, the Butler-Volmer equation is represented by two straight lines in a semilogarithmic scale, as shown in the plot below. This is what it is generally referred to as a Tafel plot.



**High-overpotential limiting case:** The Tafel behavior of the Butler-Volmer equation over a wide potential domain.

The Tafel plot is a powerful tool to derive kinetic parameters. For example, the **equilibrium potential** and the **exchange current density** are obtained at the intersection of the extrapolation of the Tafel lines at  $\eta=0$

The charge transfer coefficient is derived from the slope of the cathodic or anodic lines. It is important to note, that Tafel behaviors assumes the absence of mass transport effect.

## Mass-Transfer Limitations

For fast redox reactions the consumption of the reacting species at the interface is faster than the supply of species by mass transport and the system no longer exhibits Tafel behavior. In this case mass transport plays a dominant role in the overall kinetics of the electrochemical system. In other words, the kinetics of the redox reaction is so fast that it completely controlled by mass transport. Any cation reaching the interface is immediately reduced.

The equation that quantifies the mass transport limiting current is a combination between Faraday's and Fick's law yielding the following relationship between the current density and the concentration gradient for any  $M^{z+}/M$  couple:

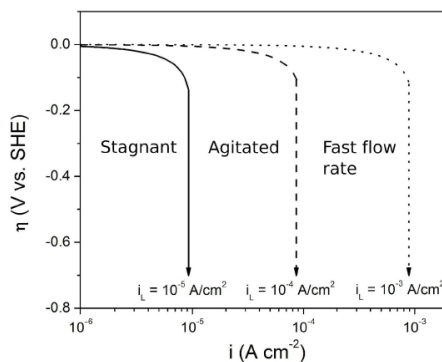
$$i = -zDF \frac{C_{\infty} - C_{int}}{\delta}$$

The current is directly proportional to the concentration gradient inside the diffusion layer.  $D$  represents the diffusion coefficient of the cation species and  $\delta$  represents the thickness of the diffusion layer.

Introducing zero interfacial concentration, the limiting current equation reduces to:

$$i_{lim} = -zDF \frac{C_{\infty}}{\delta}$$

And this is illustrated in this polarization curves below.



Also notice that the effective value of the limiting current will depend on the **hydrodynamics** of the system, which has a direct impact on the thickness of the diffusion layer.

A fast flow reduces the thickness of the diffusion layer, which in turns increase the limiting current value.

## Corrosion: Far from Equilibrium

So far, we have dealt with single-half cell reactions at equilibrium or away from  $E^{\text{eq}}$ . However, a metal in solution of its own ions is of no relevance to corrosion.

So, consider a simple corrosion experiment, a piece of iron immersed in a deaerated acid solution.

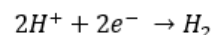
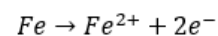
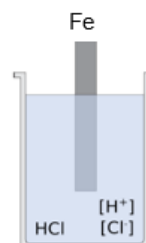
If the metal is consumed by the corrosion process, oxidation reactions are happening at the surface. Now, the principle of charge conservation dictates that the sum of all oxidation currents must equal the sum of all reduction currents to avoid the accumulation of charge on a freely immersed electrode.

Therefore, at every instant the amount of current generated by these oxidation reactions, must be balanced by cathodic a cathodic reaction. In this case the hydrogen evolution reaction.

This implies that anodic and cathodic currents must be occurring simultaneously.

Now, this is different that the scenarios that we were previously studying, this scenario does not involve a single redox reaction (forward and backward) – otherwise we would have iron dissolution and deposition balancing out and no corrosion will occur.

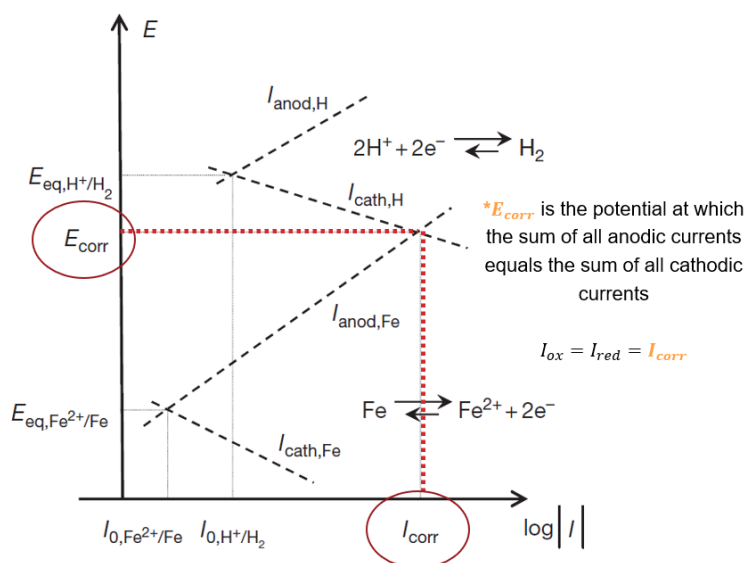
This implies that corrosion phenomena involve at least two different redox couples supplying **one** supplying the **anodic current** and the **other one** supplying the **cathodic current** to ensure the zero current balance.



$$\sum I_{\text{ox}} + \sum I_{\text{red}} = 0$$

## Evans Diagram

A useful representation for free corrosion conditions is the so-called Evans diagram, that plots potential vs current.



The main advantage of this plot is that it illustrates the two redox couples that coexist. In this case, you can see the iron couple reactions – forward and backward reactions – with the respective equilibrium potential, and the hydrogen couple as well.

The idea of mixed potential is extremely important as it indicates that the reaction with the lower equilibrium potential will be anodic and the that with the higher equilibrium potential will be cathodic.

We know in this case, that the anodic reaction is represented by the dissolution of Fe, and the cathodic reaction is represented by the evolution of hydrogen.

## Corrosion Potential

So, when these two reactions cross each other, this –self regulated coupled systems yield two fundamental parameters of the corrosion process, the **corrosion potential**,  $E_{corr}$  also called rest potential or open circuit potential (OCP) and the **corrosion current**,  $i_{corr}$ .

One thing to keep in mind is that the electrode is NOT AT EQUILIBRIUM at the  $E_{corr}$ . The metal is being oxidized and water or other oxidants are being reduced.

Additionally, the corrosion potential naturally lies between the two individual equilibrium potentials. The corrosion current means that there is an identical electron flux between the two reactions. The  $i_{corr}$  then is used to calculate the respective corrosion rate, using Faraday's law.

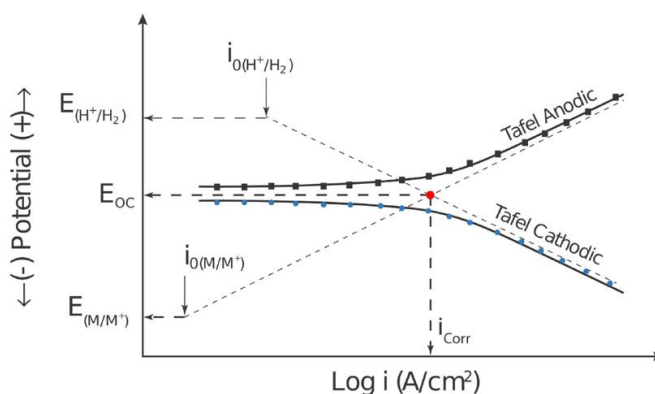
## Polarization Experiments

An equation similar in form to the Butler-Volmer equation can be derived to describe the net current curve for free corrosion systems, the **Wagner and Traud** Equation.

$$i_{net} = i_{corr} \left[ \exp \left( \frac{2.303(E - E_{corr})}{b_a} \right) - \exp \left( \frac{2.303(E - E_{corr})}{|b_c|} \right) \right]$$

The plot below shows the net current polarization curves, which is the contribution of both anodic and cathodic reactions. The dots and squares represent experimental datapoints gathered in the lab.

Notice that the difference here is that the curve is now centered around  $E_{corr}$ , rather than  $E^{eq}$  and that the current density at zero overpotential is  $i_{corr}$  rather than the exchange current density  $i_0$ .



The dots and squares indicate experimental datapoints

## Kinetics of Passivity

So far, we have seen polarization curves that follow a Tafel behavior, as you increase the overpotential the current response is linear in a logarithmic scale.

This is not always the case when we are dealing with passive metals or passive alloys. Passive metals show a distinctive potential-current density behavior.

### Passivity

Passivity is defined as a loss of electrochemical reactivity (i.e. a drastic decrease in corrosion rate) that many engineering alloys (e.g. stainless steel, Ni-based alloys, Ti and Al alloys) exhibit under certain environmental conditions.

Let's take a look at the different  $E$  and  $i$  critical parameters that fully describe a metal or alloy that shows an active to passive transition.

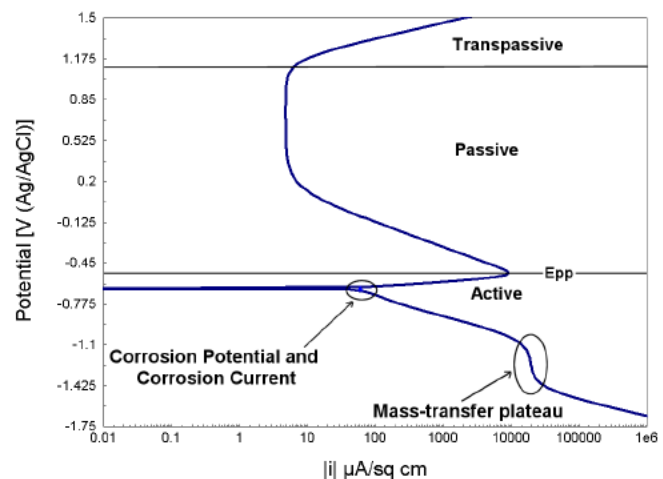
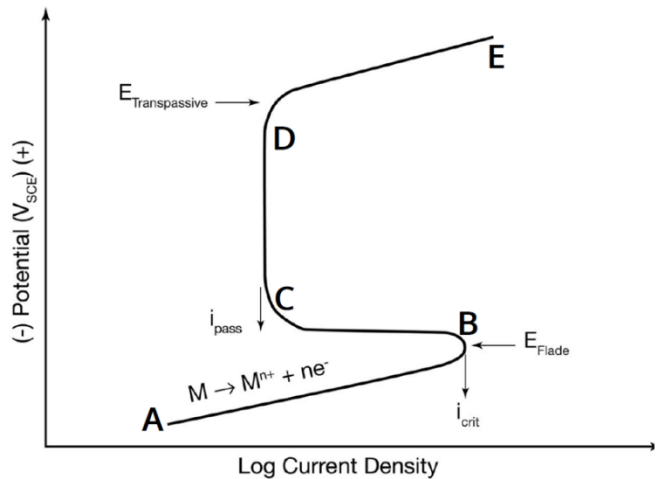
Initially the metal is in the **active state** (points A-B) the metal or alloy suffers uniform corrosion. Passivity occurs above a certain potential value called Flade Potential ( $E_{Flade}$  or  $E_{pp}$ ), point B.  $E_{Flade}$  can be reached by applying an external current or by adding a strong oxidizing agent.  $E_{Flade}$  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. A critical current density,  $i_{crit}$ , is reached at  $E_{pp}$ .

At the active-passive transition – B to C, the current density decreases by several orders of magnitude.

Passivity is maintained from point C to point D. The current density in the passive region,  $i_{pass}$ , passivation current density, is often relatively independent of potential.

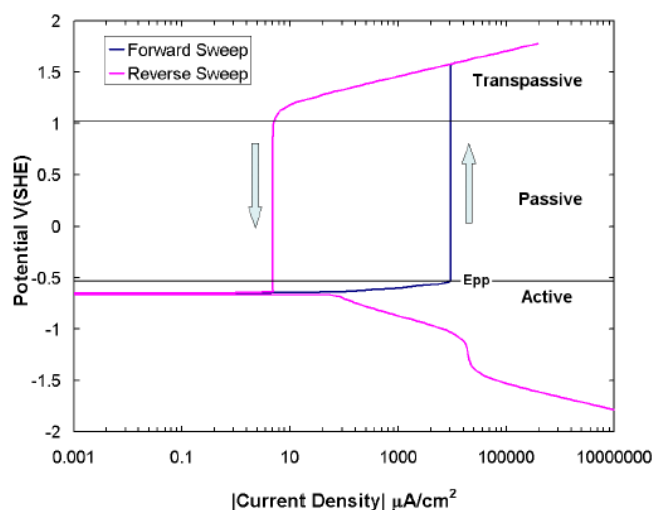
Passive films may break down at very high potentials, allowing high currents to pass again. This is called transpassive region. Transpassive dissolution occurs from points D to E. In this region there is a significant increase in current density (increased metal oxidation) as the potential becomes more positive.

A summary plot of the regions of an alloy or metal that displays active-to-passive behavior: Active, Passive and Transpassive is shown in the plot to the right.



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. The below figure 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.



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 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.

## Net Current – Adding more reactions

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.

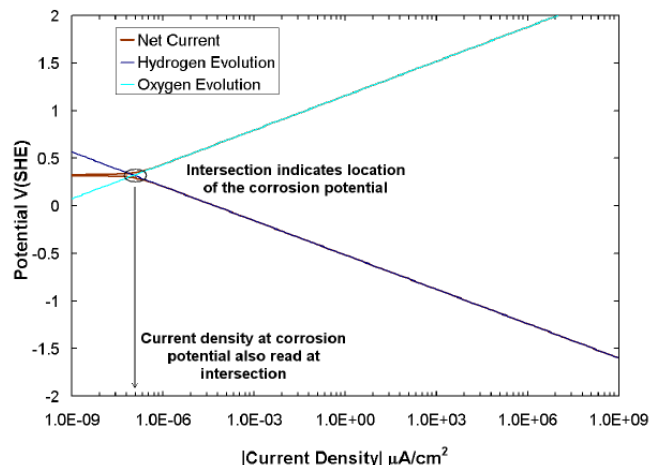
Since the software is valid only within the constraints of aqueous systems, the polarization curves will be bounded by water decomposition reactions. At sufficiently positive potential, the oxygen evolution reaction will occur:



and at sufficiently negative potentials the hydrogen reaction occurs



The 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*.

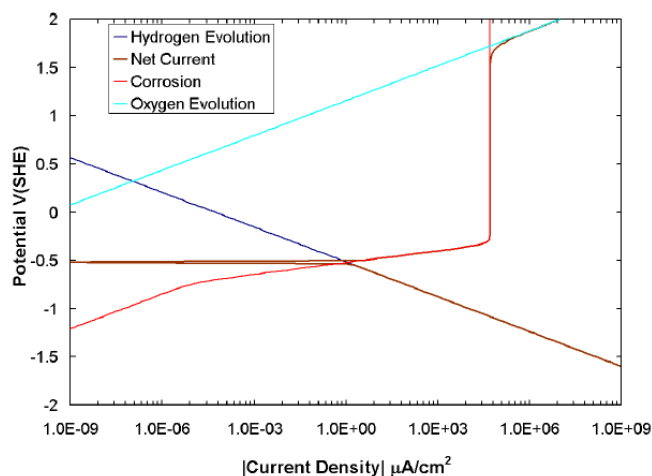


Basic polarization curve with water decomposition reactions

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



Adding a line for reaction (3) and adjusting the net current to include the new reaction, produces the plot below.



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,  $i_o$ , 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.

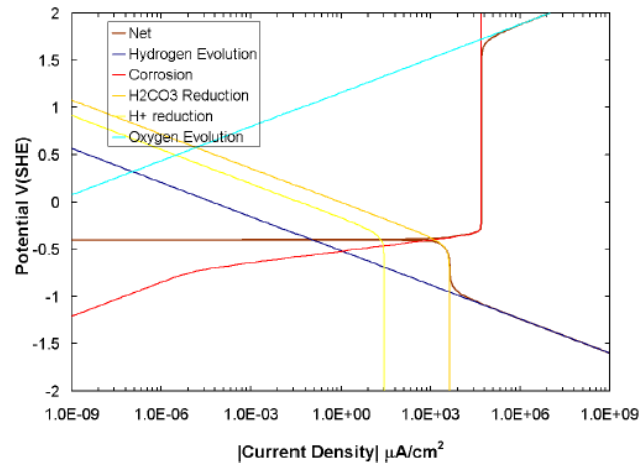
Adding  $H_2CO_3$  to the fluid in contact with the metal adds 2 more reactions:





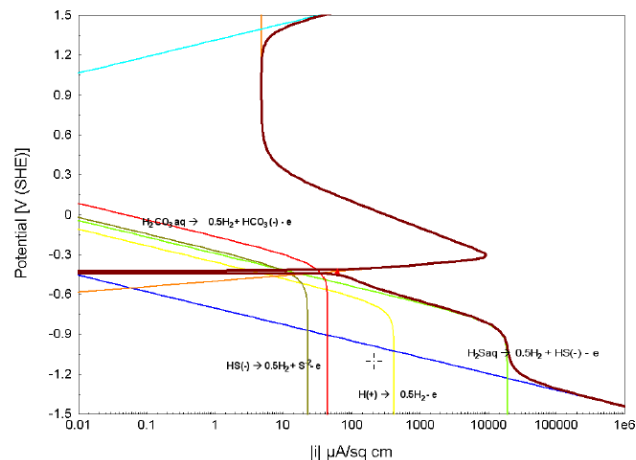
Both of these reactions will have mass transfer effect limitations.

The below figure shows the addition of reactions (4) and (5) to the model. The addition pushes up the rate of corrosion and moves the corrosion potential towards a more anodic value.



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

As more components are added, more reactions influencing corrosion may be added to the mixed potential expression. For instance, the figure below shows that the addition of H<sub>2</sub>S to the system at conditions of saturation and higher temperature. Also note that the changes in conditions affect the corrosion (anodic) polarization shape.



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

## Net current – polarization curve

Of all the curves plotted by OLI Studio: Corrosion Analyzer, only the 'net current' is experimentally measurable. This net current is the addition of all the current contributions of all anodic and cathodic reactions at a specific potential, and it is represented by the thick red line in the plot above. 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.

The above plot 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.

## Galvanic couple

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.

## 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.

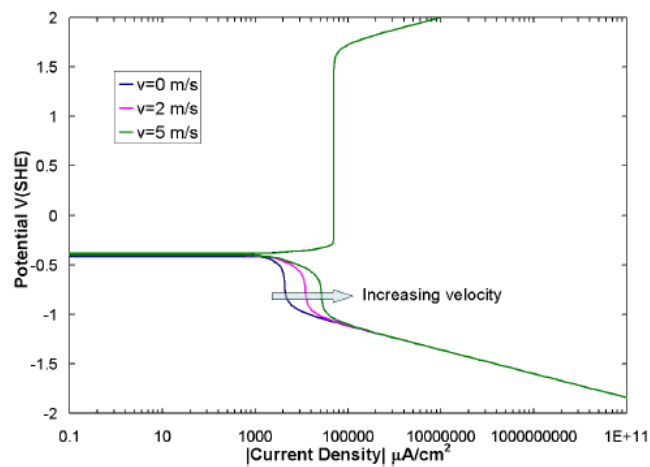
The above plot shows three reactions where hydrogen ions are consumed at the metal surface, and none are produced. As the mass transfer limitation is approached, the pH will rise because fresh hydrogen ions will not be able to diffuse fast enough to replace what is lost through the partial processes.

## Fluid Dynamics

As seen so far, the corrosive species must come from the bulk aqueous phase before it can react at the metal surface. 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.

A known fluid velocity profile is needed, 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



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

The above figure 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.

## Chapter IV – Corrosion Rates and Polarization Curves (Exercises)

### 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

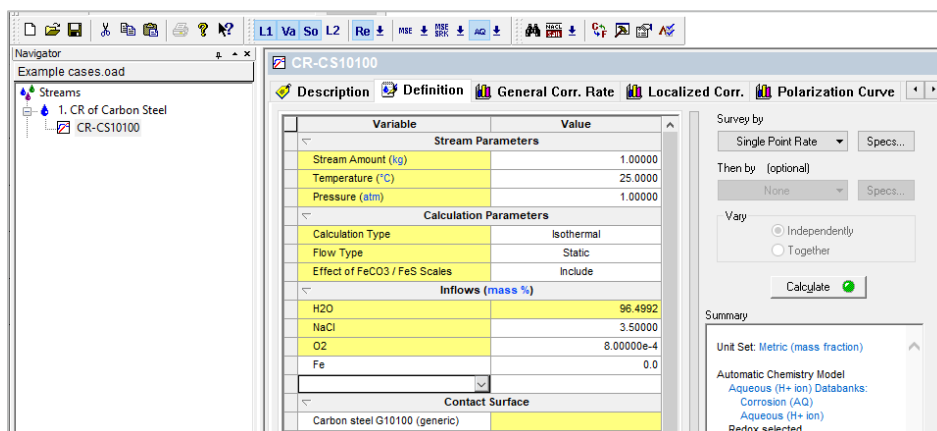


- ✓ To start the software, double-click the OLI Studio icon on the desktop, which will take you to the OLI Studio interface where you can start creating your calculations.

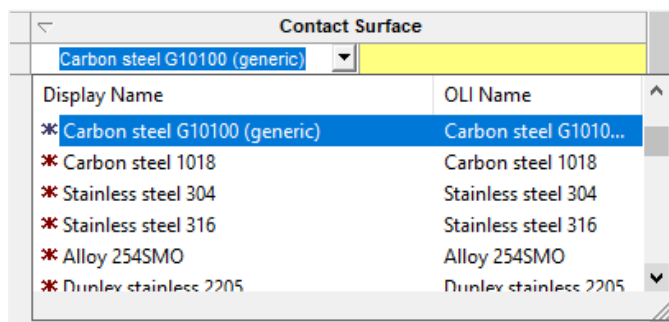
Use the inputs and parameters from the table below to create the stream's composition. Certain inputs, such as the name style, units, etc. will require further adjustments, and will be described as necessary.

Corrosion Rate Calculation			
Calculation Settings		Stream Composition and Conditions	
Stream Name	CR of carbon steel	Stream Amount	1 kg
Name Style	Display Formula	Temperature	25 °C
Unit Set	Metric, Batch, Mass Frac.	Pressure	1 atm
Framework	AQ	H2O	Calculated
Calculation Type	Corrosion Rates	O2	8e-4 wt%
Contact Surface	Carbon Steel G10100 (generic)	NaCl	3.5 wt%

- ✓ 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, Mass Frac.
- ✓ 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.

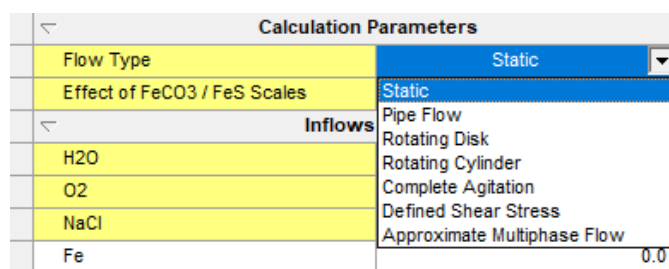


**Note:** By default, the software has selected **Carbon steel G10100 (generic)** as the default contact surface to perform the corrosion rates on. You can click on the white space of the **Carbon steel G10100 (generic)** name, and it will show a drop-down arrow. You can then click on the dropdown arrow, 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.

#### *Defined Shear Stress*

In this calculation, the user enters the value of the shear stress if it can be obtained from a separate fluid dynamics program. The shear stress is then used to calculate mass transfer limitations.

A user can also directly input the value of the shear stress if they can obtain it from a separate fluid dynamics program.

#### *Approximate Multiphase Flow*

In this calculation, a correlation for shear stress is used. The shear stress is then used to calculate mass transfer limitations. The input parameters for calculation of wall shear stress are the following:

Parameter	Default Value	Range
Pipe diameter	10 cm	0 to $\infty$
Liquid Flow in Pipe	0.01 m <sup>3</sup> /s	
Gas Flow in Pipe	0.01 m <sup>3</sup> /s	
Pipe Roughness	0.04 cm	0 to 100
Absolute viscosity, 2 <sup>nd</sup> Liquid (Oil phase)	10 cP	
Water Cut at Point of Dispersion Inversion, $\phi_c$	0.5	0.3 to 0.9
Maximum Relative Liquid Viscosity of Dispersion at Inversion	7.06	1 to 100

- ✓ 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.

The screenshot shows the 'Survey by' dropdown menu on the right, which is open and displays a list of options: Single Point Rate (selected), Temperature, Pressure, Composition, pH, Pipe Flow, Rotating Disk, Rotating Cylinder, Thermal Aging Temp., Thermal Aging Time, Shear Stress, and Liquid Flow in Pipe. Below the menu, it says 'Redox selected'.

On the left, there is a table with two columns: 'Variable' and 'Value'. The table is organized into sections: 'Stream Parameters', 'Calculation Parameters', 'Inflows (mass %)', and 'Contact Surface'. The 'Stream Parameters' section includes Stream Amount (kg) at 1.00000, Temperature (°C) at 25.0000, and Pressure (atm) at 1.00000. The 'Calculation Parameters' section includes Calculation Type (Isothermal), Flow Type (Static), and Effect of FeCO<sub>3</sub> / FeS Scales (Include). The 'Inflows (mass %)' section includes H<sub>2</sub>O (96.4992), NaCl (3.50000), O<sub>2</sub> (8.00000e-4), and Fe (0.0). The 'Contact Surface' section includes Carbon steel G10100 (generic).

**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.

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

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

*Rotating Cylinder Survey*


*Thermal Aging Temp. Survey*

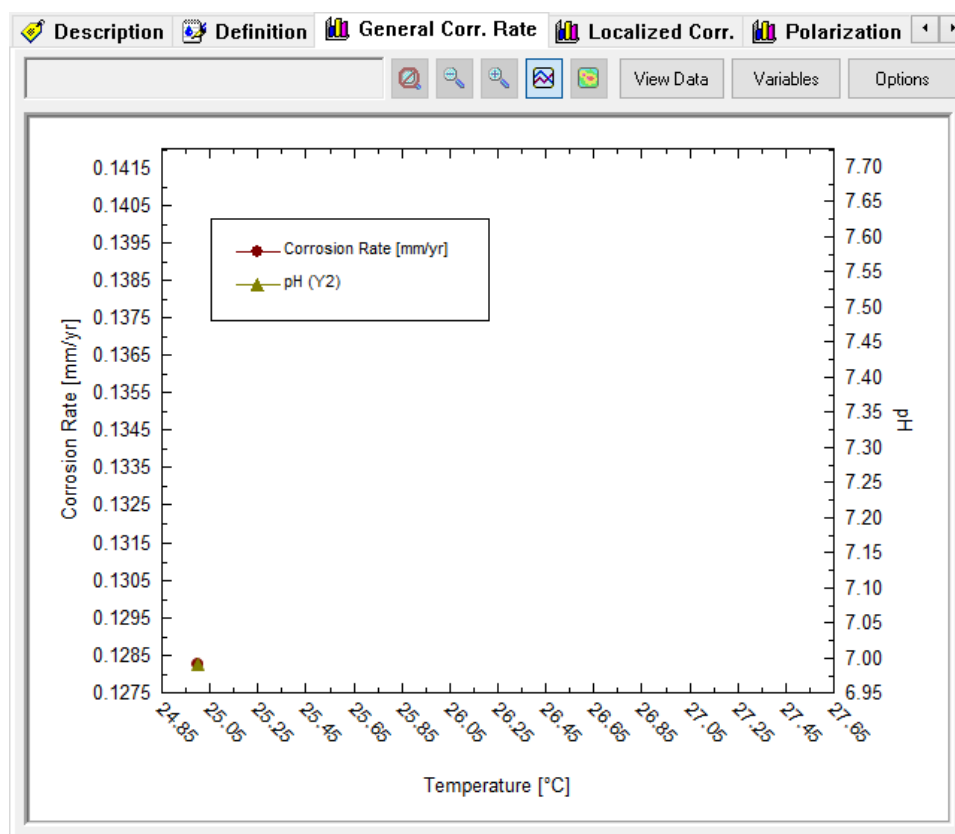
*Thermal Aging Time Survey*

*Liquid Flow in Pipe Survey*

- ✓ 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.



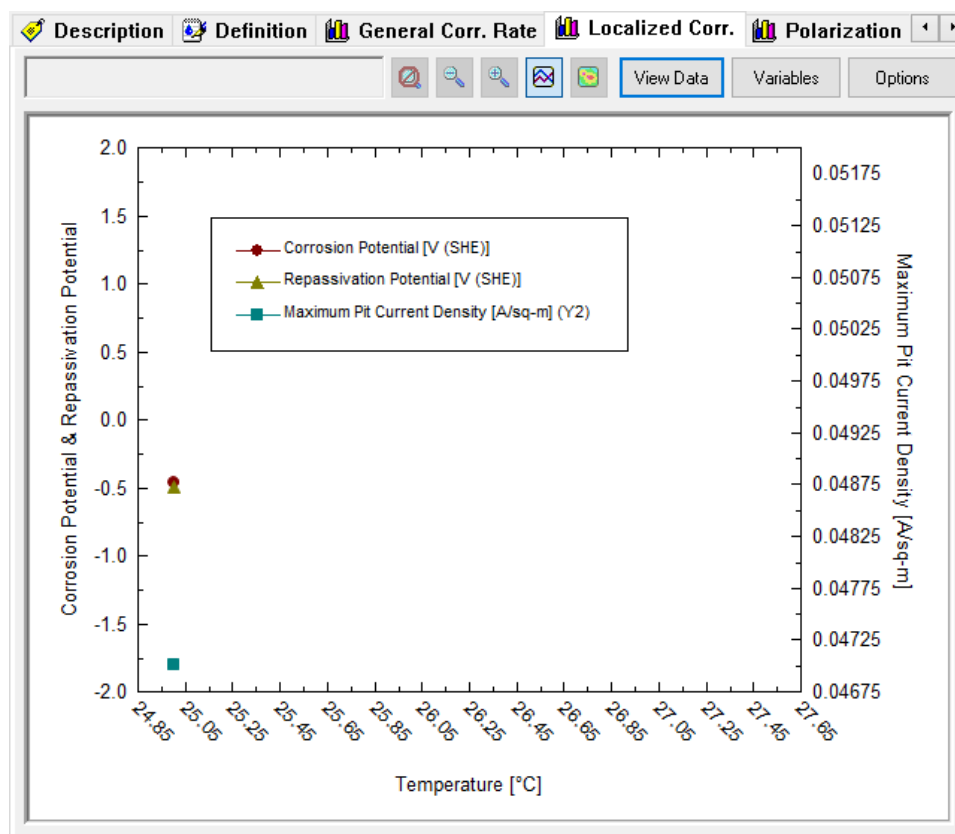
- ✓ **Click** on the **View Data** button to see the results in tabulated form.

	Temperature	Corrosion Rate	pH
	°C	mm/yr	
1	25.0000	0.128276	6.99047

The predicted corrosion rate of carbon steel at 25 °C and 1 atm is ~0.13 mm/year when exposed to an oxygenated 3.5 wt% 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)

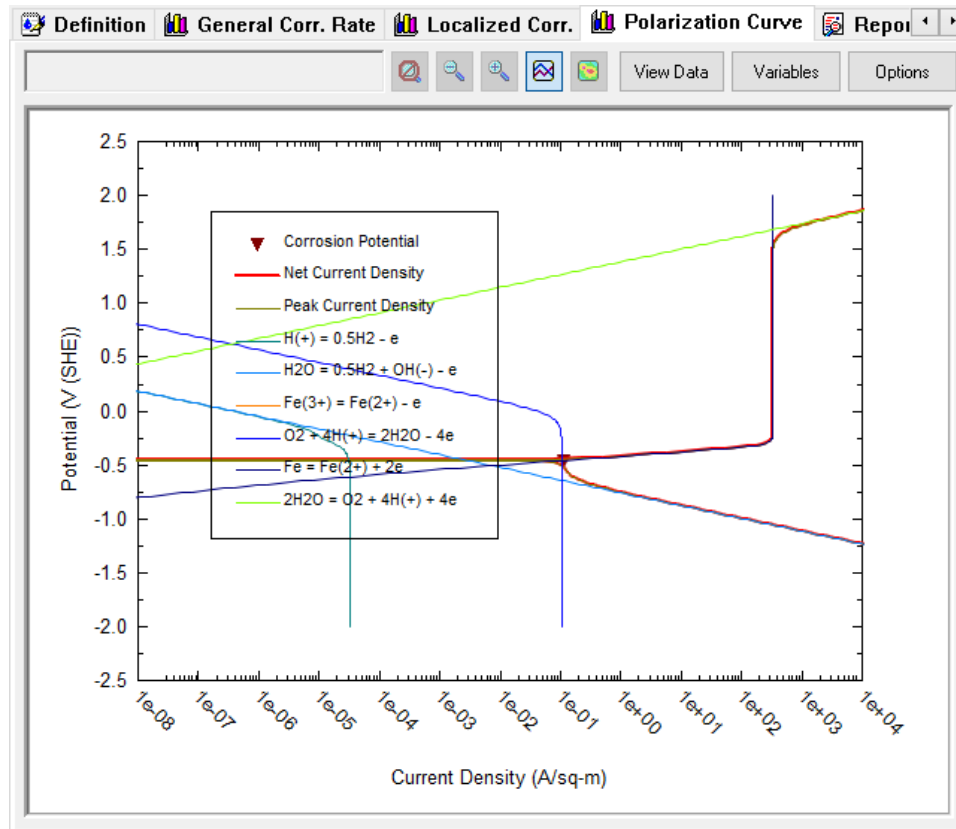


- ✓ Click on the **View Data** button to see the results in tabulated form.

	Temperature	Corrosion Potential	Repassivation Potential	Maximum Pit Current Density
	°C	V (SHE)	V (SHE)	A/sq-m
1	25.0000	-0.459348	-0.499125	0.0470063

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 3.5 wt% 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.

## Neutralizing a 1 m Acetic Acid solution

The presence of organic acids found in produced water has been reported as a severe concern in mild steel pipeline corrosion for the oil and gas industry. Among organic acids, acetic acid is known as the dominant low molecular weight acid found in produced fluids. According to many studies, acetic acid enhances the corrosion rate of mild steel by accelerating the cathodic reaction. Let's compute the corrosion rate of 1 m Acetic acid solution, analyze the impact of the cathodic reactions, and compare it to the corrosion rate of a neutralized solution.

### Corrosion rate of a 1 m Acetic Acid solution

#### Starting the Simulation

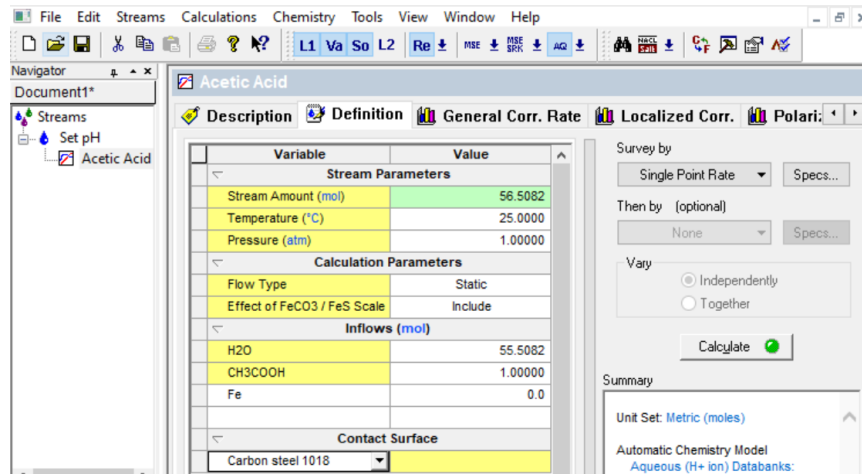


- ✓ To start the software, double-click the OLI Studio icon on the desktop, which will take you to the OLI Studio interface where you can start creating your calculations.

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	Set pH	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	Acetic Acid	1 mole
Contact Surface	Carbon Steel G10100 (generic)		

- ✓ Add a new **Stream**
- ✓ **Click** on the new Stream and press **<F2>** to change the name to **Set pH**
- ✓ 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
- ✓ **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.
- ✓ Rename the corrosion rate calculation as **Acetic Acid - Isothermal**
- ✓ Select alloy **Carbon steel 1018** as the contact surface



- ✓ 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.

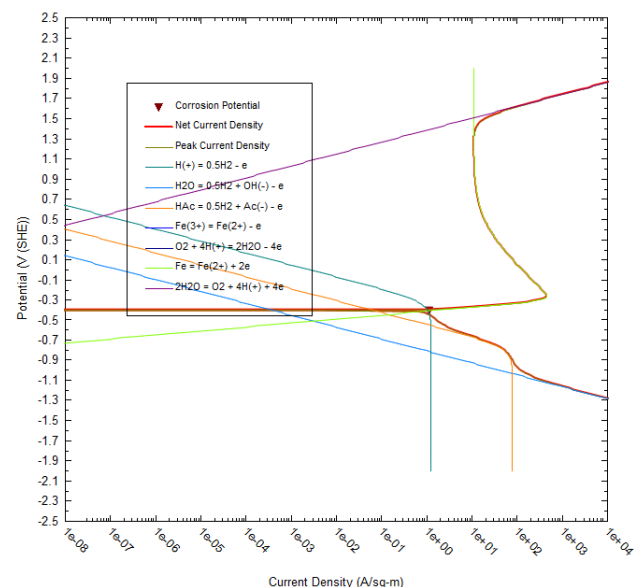
	Temperature	Corrosion Rate	pH
	°C	mm/yr	
1	25.0000	1.31629	2.39694

The predicted corrosion rate of carbon steel at 25 °C and 1 atm is approx. 1.32 mm/year when exposed to a 1 m Acetic Acid solution.

- ✓ Click on the **Polarization Curve** tab. 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.

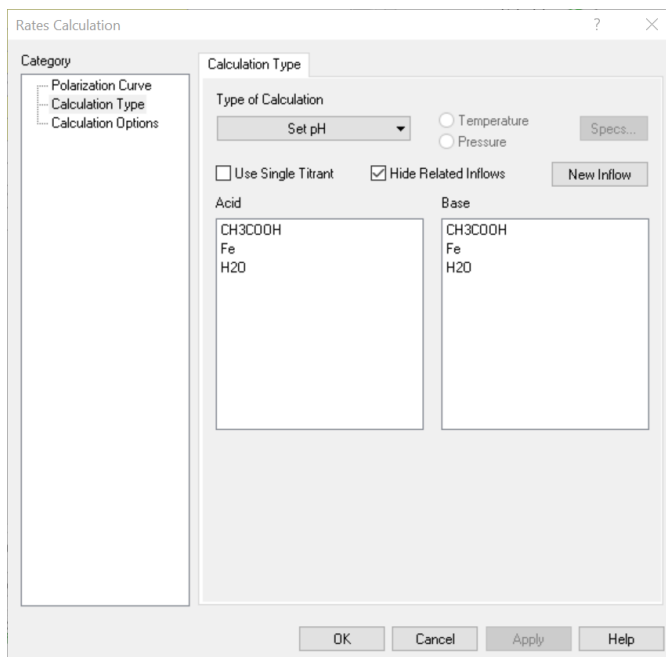
Notice that two cathodic reactions play a significant role on the corrosion rate process: the hydrogen reduction reaction (turquoise line) and the acetic acid reduction reaction (orange line).



## Corrosion rate of a 1 m Acetic Acid neutralized solution

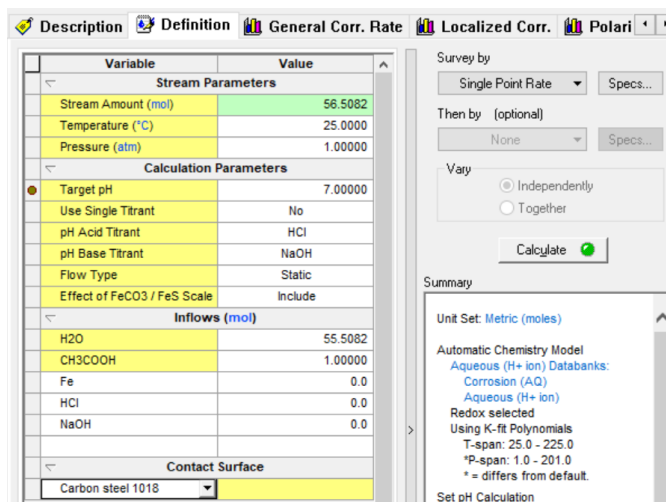
Now, we want to study the corrosion rate of the same solution but now neutralized to pH=7.

- ✓ Go to the **Add Calculation** button and select **Corrosion Rates** to add a new corrosion rate calculation
- ✓ Rename the corrosion rate calculation as **Acetic Acid – Neutralized**
- ✓ Go to the **Survey by** option and select **Single Point Rate**
- ✓ Click on the **specs...** button and this will open a new window and select the **calculation type** in the category section
- ✓ In the **type of calculation** selection option, select **set pH** and then click **OK**



The 'Rates Calculation' dialog box is shown. On the left, the 'Category' list includes 'Polarization Curve', 'Calculation Type', and 'Calculation Options'. The 'Calculation Type' tab is active. Under 'Type of Calculation', 'Set pH' is selected in the dropdown. There are radio buttons for 'Temperature' and 'Pressure'. A 'Specs...' button is to the right. Below these are checkboxes for 'Use Single Titrant' (unchecked) and 'Hide Related Inflows' (checked), with a 'New Inflow' button. Two list boxes are present: 'Acid' containing 'CH3COOH', 'Fe', and 'H2O'; and 'Base' containing 'CH3COOH', 'Fe', and 'H2O'. At the bottom are 'OK', 'Cancel', 'Apply', and 'Help' buttons.

- ✓ A new section for adjusting pH under the **calculation parameters** section appears.
- ✓ Change the **target pH** to 7.0




The 'General Corr. Rate' dialog box is shown. It has tabs for 'Description', 'Definition', 'General Corr. Rate', 'Localized Corr.', and 'Polarization'. The 'General Corr. Rate' tab is active. It features a table with 'Variable' and 'Value' columns. The table is divided into sections: 'Stream Parameters' (Stream Amount: 56.5082, Temperature: 25.0000, Pressure: 1.00000), 'Calculation Parameters' (Target pH: 7.00000, Use Single Titrant: No, pH Acid Titrant: HCl, pH Base Titrant: NaOH, Flow Type: Static, Effect of FeCO3 / FeS Scale: Include), 'Inflows (mol)' (H2O: 55.5082, CH3COOH: 1.00000, Fe: 0.0, HCl: 0.0, NaOH: 0.0), and 'Contact Surface' (Carbon steel 1018). On the right, there are 'Survey by' (Single Point Rate) and 'Then by (optional)' (None) dropdowns, 'Vary' radio buttons (Independently selected), and a 'Calculate' button. A 'Summary' section at the bottom right shows 'Unit Set: Metric (moles)' and 'Automatic Chemistry Model' details.

Variable	Value
<b>Stream Parameters</b>	
Stream Amount (mol)	56.5082
Temperature (°C)	25.0000
Pressure (atm)	1.00000
<b>Calculation Parameters</b>	
Target pH	7.00000
Use Single Titrant	No
pH Acid Titrant	HCl
pH Base Titrant	NaOH
Flow Type	Static
Effect of FeCO3 / FeS Scale	Include
<b>Inflows (mol)</b>	
H2O	55.5082
CH3COOH	1.00000
Fe	0.0
HCl	0.0
NaOH	0.0
<b>Contact Surface</b>	
Carbon steel 1018	

- ✓ Change the Select alloy **Carbon steel 1018** as the contact surface


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

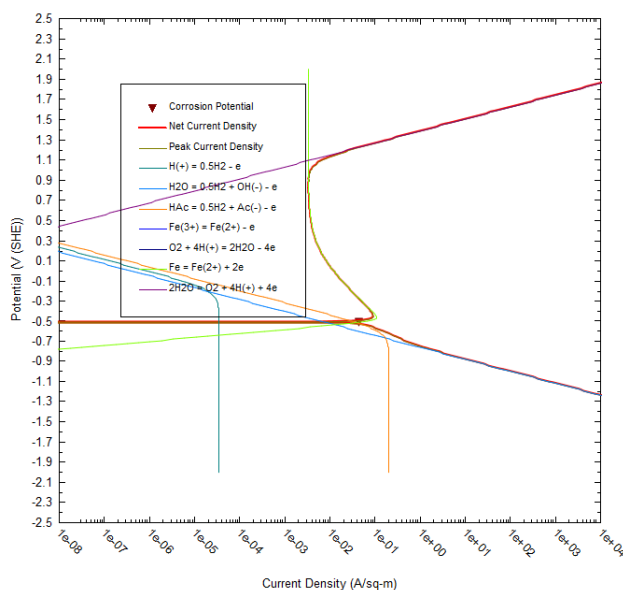
## Analyzing the Results

- ✓ Notice that the software added 0.997023 moles of NaOH as the base titrant to neutralize the pH to 7.0.
- ✓ 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	0.0519212	7.00000

The predicted corrosion rate of carbon steel at 25 °C and 1 atm is approx. 0.052 mm/year when exposed to a neutralized 1 m Acetic Acid solution. The corrosion rate decreased by two orders of magnitude.

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



By increasing the pH two effects can be seen in the polarization curve. 1. The anodic polarization response displays lower current density values and 2. the main cathodic reaction that contributes to the corrosion potential is the acetic acid reduction reaction (orange curve) followed by the reduction reaction of water (light blue curve). The hydrogen reduction reaction no longer plays a significant role on the corrosion process since the pH was neutralized.

# 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 (DEA) is used to neutralize an acid gas containing carbon dioxide (CO<sub>2</sub>) and hydrogen sulfide (H<sub>2</sub>S). The DEA 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 investigate the gas condensate composition and then perform a Corrosion Rate calculation with it. 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	100 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

First, let confirm is this stream is all in the gas phase

- ✓ Go to the **Add Calculation** button
  - Select **Single Point** calculation

- ✓ Select **Isothermal** as Type of Calculation
  - Name it **Isothermal Calculation**
- ✓ Now, we are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key

Your screen should look like the image below.

Variable	Value
<b>Stream Parameters</b>	
Stream Amount (mol)	100.000
Temperature (°C)	38.0000
Pressure (atm)	1.20000
<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

**Summary**

Unit Set: <Custom>

Automatic Chemistry Model  
 Aqueous (H+ ion) Databanks:  
 Aqueous (H+ ion)  
 Using K-fit Polynomials  
 T-span: 25.0 - 225.0  
 \*P-span: 1.0 - 201.0  
 \* = differs from default.

Isothermal Calculation  
 38.0000 °C 1.20000 atm

Phase Amounts

Aqueous	0.0 mol
Vapor	100.000 mol
Solid	0.0 mol

We have confirmed that stream is 100% in the vapor phase. Unfortunately, we cannot perform corrosion rate calculations on a stream that is 100% vapor. The corrosion model needs to an aqueous phase to calculate corrosion rate values.

The operators know that a liquid phase is condensing out of this vapor stream. So, there are two ways to calculate the liquid condensate:

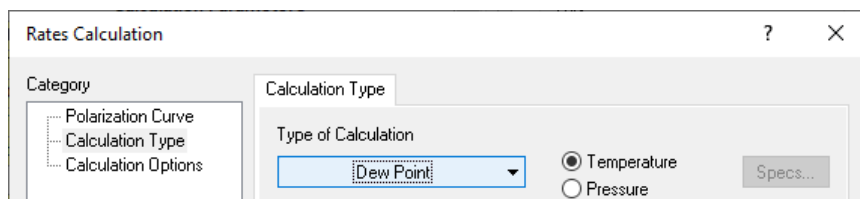
1. Calculate the temperature at which the gas condensate forms (dew temperature) and determine the composition of the condensate
2. Simulate the saturation of the gas with water vapor and calculate the composition of the condensate that forms

Let's start with the first approach: Calculate the dew point temperature at which a gas condensate will form.



# 1. Dew Point Temperature

- ✓ Under the *Gas Condensate* stream, go to the **Add Calculation** button and select **Corrosion Rates** calculation
- ✓ **Go** to the **Survey by** option and select **Single Point Rate**. Change the name to **Gas Cond. Dew Point T**
- ✓ **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**.



- ✓ **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

Variable	Value
<b>Stream Parameters</b>	
Stream Amount (mol)	100.000
Temperature (°C)	38.0000
Pressure (atm)	1.20000
<b>Calculation Parameters</b>	
Calculation Type	Dew Point
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)	

**Summary**

Unit Set: <Custom>

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 - 201.0  
 \* = differs from default.


Dew Point Calculation  
 1.20000 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

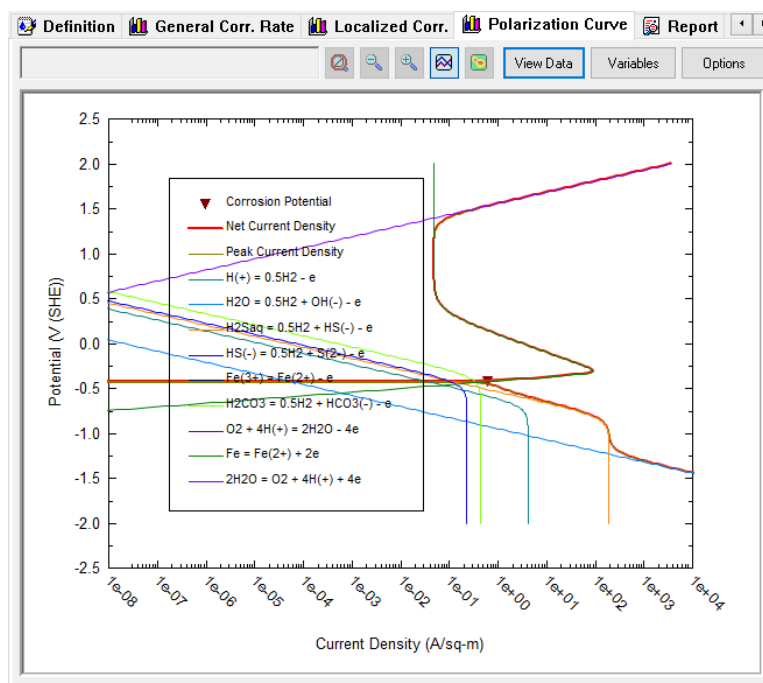
- ✓ Now, we are ready to perform the calculation. **Click** on the **Calculate** button
- ✓ It is time to **save** your file (**File > Save as...**) or using the **save** icon in the tool bar. You can save it under the same file created in the previous example named *Corrosion Rates*.

### 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.

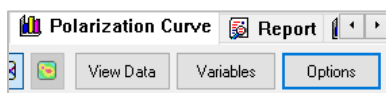
	Temperature	Corrosion Rate	pH
	°C	mill/yr	
1	37.5872	27.7479	3.92733

- ✓ Notice that the calculated dew temperature is 37.6°C, corrosion rate is 27.75 mil/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 )

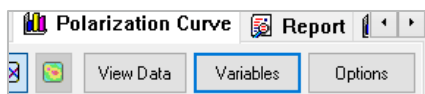


Before interpreting this plot, we will format it for easy viewing.

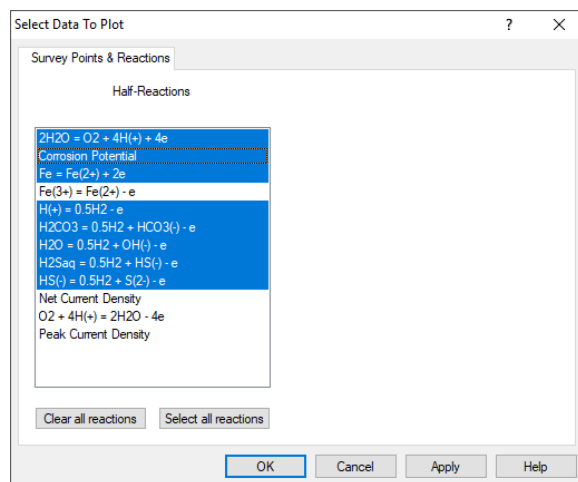
- ✓ Click on the **Options** button. This will open a new window.



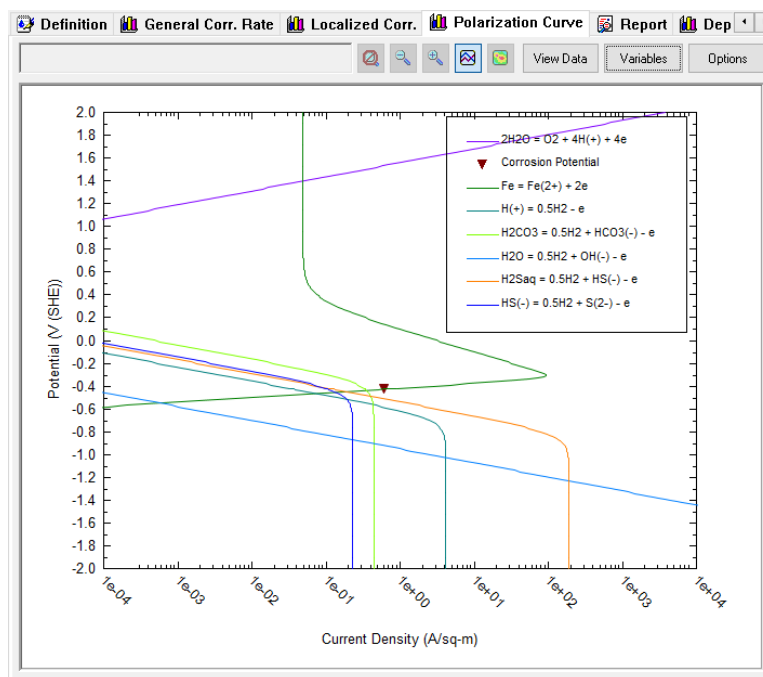
- ✓ Under the **Category** section select **X axis**. Change the **Minimum** to 1e-4 and **Maximum** to 1e4.
- ✓ Now, select **Y axis**. Change the **Minimum** to -2.0 and **Maximum** to 2.0. Then **click OK**.
- ✓ Click on the **Variables** button. This will open a new window.



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



- ✓ Your polarization curve should look like the image below.



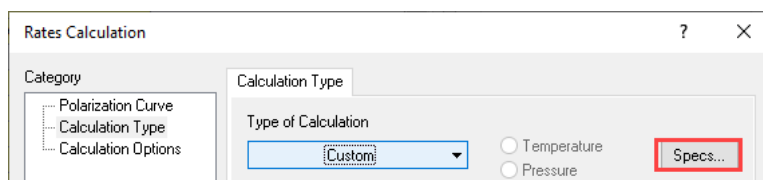
You can click and drag the legend of the polarization curve to the desired position.

This is a measured potential vs. current density plot. The anodic portion (**green curve**) is the carbon steel. The rest 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.

## 2. Saturating the Gas with Water

- ✓ Under the *Gas Condensate* stream, go to the **Add Calculation** button and select **Corrosion Rates**
- ✓ Go to the **Survey by** option and select **Single Point Rate**. Change the name to **Saturating Gas w/ Water**
- ✓ 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**.



- ✓ Click on the **Specs...** button to open the custom variables window
  - ✓ Go to the Variables to Fix – select **Moles (True) – Aqueous**
  - ✓ Go to the Variables to Free – select **H2O**
- ✓ Click **OK** to close the windows
- ✓ Under the **Calculation Parameters** section define the **Target** values as shown in the image below

Calculation Parameters	
Calculation Type	Custom
Target: Moles (True) – Aqueous (mol)	1.00000e-6
Adjusted: H2O (mole %)	5.00000

What we have instructed the software was to manipulate the amount of water (the adjusted variable) in the system such that the gas gets saturated with water. The software will add water to the system until a small amount of liquid forms, i.e., the first drop of water condensates which we have defined as  $1\text{e-}6$  moles.

- ✓ **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

Variable	Value
<b>Stream Parameters</b>	
Stream Amount (mol)	100.000
Temperature (°C)	38.0000
Pressure (atm)	1.20000
<b>Calculation Parameters</b>	
Calculation Type	Custom
Target: Moles (True) - Aqueous (mol)	1.00000e-6
Adjusted: H2O (mole %)	5.00000
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

Survey by: Single Point Rate Specs...  
 Then by (optional): None Specs...  
 Vary: ☐ Independently ☐ Together  
Calculate

Summary:  
 Unit Set: <Custom>

- ✓ Now, we are ready to perform the calculation. **Click** on the **Calculate** button
- ✓ 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 output tab named **1** (highlighted in the red box in the image below) to see the results

Definition
General Corr. Rate
Localized Corr.
Polarization Curve
Report
Deplet

Variable	Value
<b>Stream Parameters</b>	
Stream Amount (mol)	100.129
Target: Moles (True) - Aqueous (mol)	1.00000e-6
Moles (True) - Vapor (mol)	100.129
Temperature (°C)	38.0000
Pressure (atm)	1.20000
<b>Calculation Results</b>	
Target: Moles (True) - Aqueous (mol)	1.00000e-6
Adjusted: H2O (mole %)	1.66310
<b>Corrosion Values</b>	
Repassivation Potential (V (SHE))	99.9000
Corrosion Rate (mm/yr)	0.709039
Corrosion Potential (V (SHE))	-0.427438
Corrosion Current Density (A/sq-m)	0.611478
<b>Inflows (mole %)</b>	
Adjusted: H2O	5.54202
CO <sub>2</sub>	77.3001
N <sub>2</sub>	0.0199742
H <sub>2</sub> S	16.5786
CH <sub>4</sub>	0.499355
C <sub>2</sub> H <sub>6</sub>	0.0299613
C <sub>3</sub> H <sub>8</sub>	0.0299613
<b>Contact Surface</b>	
Carbon steel G10100 (generic)	

Survey by: Single Point Rate Specs...  
 Then by (optional): None Specs...  
 Vary: ☐ Independently ☐ Together  
Calculate

Summary:  
 Unit Set: <Custom>  
 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 - 201.0  
 \* = differs from default.  
 Custom Calculation  
 Fixed variable:  
   Moles (True) - Aqueous, target:  
     1.00000e-6 mol  
 Free variable:  
   H2O, total:  
     5.54202 mole %  
 Calculation complete  
 Single Point  
 No secondary survey selected

Input 1
Advanced Search Add as Stream Export

The software calculates that the saturated gas stream has a water composition of 5.54 mole%. We also know that a small amount of liquid phase was formed (1e-6 moles). The composition of the liquid phase is the one that we are interested in since it is this phase that causes corrosion attack.

- ✓ Right click on any gray area of the output table and select **Sections > Aqueous**. This will enable the aqueous phase section and its respective composition.

2.3. Saturating Gas w/ Water

Definition General Corr. Rate Localized Corr. Pr

Variable	Value
<b>Stream Parameters</b>	
Stream Amount (mol)	100.12
Target: Moles (True) - Aqueous (mol)	1.00000e
Moles (True) - Vapor (mol)	100.12
Temperature (°C)	38.00
Pressure (atm)	1.200
<b>Calculation Results</b>	
Target: Moles (True) - Aqueous (mol)	1.00000e
Adjusted: H2O (mole %)	1.663
<b>Corrosion Values</b>	
Repassivation Potential (V (SHE))	99.90
Corrosion Rate (mm/yr)	0.7090
Corrosion Potential (V (SHE))	-0.4274
Corrosion Current Density (A/sq-m)	0.6114
<b>Inflows (mole %)</b>	
Adjusted: H2O	5.542
CO2	77.30
N2	0.01997
H2S	16.57
CH4	0.4993
C2H6	0.02996
C3H8	0.02996
<b>Contact Surface</b>	
Carbon steel G10100 (generic)	

Input 1

Advanced Search

Units Manager...  
Save default layout  
Generate Model  
Hide Zero Values  
Sections

- Stream Parameters
- Calculation Results
- Corrosion Values
- Inflows
- Related Inflows
- Additional Stream Parameters
- Phase Flow Properties
- Thermodynamic Properties
- Pre-scaling Tendencies
- Pre-scaling Index
- Scaling Tendencies
- Scaling Index
- Aqueous**
- Vapor
- Solid
- Molecular Apparent - Aqueous
- Totals
- Molecular Totals
- MBG Totals
- Activity Coefficients
- Fugacity Coefficients
- Fugacities - Vapor
- K-Values
- Gibbs Free Energy
- Gibbs Free Energy Standard State (x-based)
- Entropy
- Entropy Standard State (x-based)
- Mobilities
- Self Diffusivities
- Partial Pressures
- Contact Surface

Scroll down to see the results

Inflows (mole %)	
Adjusted: H2O	5.54202
CO2	77.3001
N2	0.0199742
H2S	16.5786
CH4	0.499355
C2H6	0.0299613
C3H8	0.0299613
Aqueous (mole %)	
H2O	99.9312
CO2	0.0410008
H2S	0.0273106
H+1	2.14901e-4
HCO3-1	1.80516e-4
HS-1	3.43843e-5
CH4	1.29258e-5
C2H6	8.57476e-7
C3H8	6.67227e-7
N2	2.41929e-7
OH-1	3.92345e-10
CO3-2	9.30893e-11
S-2	9.22096e-14
H2	8.33569e-30
O2	5.86128e-30

Notice that the liquid composition has dissolved CO<sub>2</sub> and H<sub>2</sub>S in it, 0.04 mole% and 0.027 mole%, respectively.

✓ 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	mil/yr	
1	38.0000	27.9149	3.92872

Notice that at 38°C, the calculated corrosion rate is 27.9 mil/year, the pH of the condensed phase is 3.93. These values are very similar to the previous dew point temperature calculation.

This general corrosion rate value is high, and it is due to the CO<sub>2</sub> and H<sub>2</sub>S species that are being portioned from the gas phase to the aqueous phase, causing a low pH value. We would need to explore mitigation strategies.

### Mitigation Strategies

There are several mitigating solutions to this corrosion problem. One is adding insulation to prevent temperature drops. However, the dew point temperature 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.

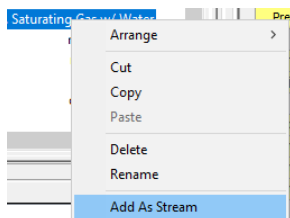
Changing the chemistry to change the partial oxidation and reduction processes is also an option. Changing alloys could mitigate the corrosion problems as well. We will explore the change of chemistry and change of alloys for this example.

### Adjusting the solution chemistry

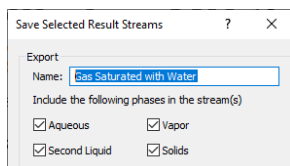
The condensate pH is approximately 3.9. We can try to add a base to increase the pH. In this section, we will add Diethanolamine to raise the pH to 7.5.

### Single Point– Set pH Calculation

- ✓ Click on the '*Saturating Gas with water*' corrosion rate calculation and **Right click** on it, and select the option **Add As Stream**



- ✓ This will open a new window
- ✓ Change the name to **Gas Saturated with Water** and click **OK**



A new stream should have been created and added to the Navigator panel list.

- ✓ Select the stream **Gas Saturated with Water** and go to the **Add Calculation** button and select **Corrosion Rates**
- ✓ Select **Single Point Rate** as the Survey by calculation
- ✓ Change the name to **Neutralizing with 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 Calculation Type** option under the **Calculation Parameters** section and change the calculation from **Isothermal** to **Set pH**

Note: To enable the drop-down list, simply on the Isothermal white cell, and then you will see the drop-down option.

Calculation Parameters	
Calculation Type	Set pH
Target pH	Isothermal
Use Single Titrant	Bubble Point
pH Acid Titrant	Dew Point
pH Base Titrant	Vapor Amount
Flow Type	Vapor Fraction
	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.

Calculation Parameters	
Calculation Type	Set pH
Target pH	7.500
Use Single Titrant	No
pH Acid Titrant	HCL
pH Base Titrant	HN(C2H4OH)2
Flow Type	N2
Effect of FeCO3 / FeS Scales	H2S
	CH4
	C2H6
	C3H8
	H2
	O2
	Fe
	HN(C2H4OH)2

- ✓ Change **Flow Type** to **Pipe Flow** (Leave the default values of pipe diameter= 10 cm and pipe flow velocity of 2 m/s)
- ✓ Leave the default alloy **Carbon steel G10100 (generic)** as the contact surface

Your screen should look like the image below.

Calculation Parameters	
Calculation Type	Set pH
Target pH	7.50000
Use Single Titrant	No
pH Acid Titrant	HCL
pH Base Titrant	HN(C2H4OH)2
Flow Type	Static
Effect of FeCO3 / FeS Scales	Include
Inflows (mole %)	
H2O	5.54202
CO2	77.3001
N2	0.0199742
H2S	16.5786
CH4	0.499355
C2H6	0.0299613
C3H8	0.0299613
H2	5.14186e-25
O2	2.57093e-25
Fe	0.0
HN(C2H4OH)2	0.0
Contact Surface	
Carbon steel G10100 (generic)	




Note: The calculate button may turn on yellow, indicating that some species were not used to calibrate the corrosion model, however, you can still proceed with the calculation.

- ✓ 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.

The pH is set to 7.5 and the inflow of DEA to the total gas is approximately 3.1e-3 mole%.

- ✓ 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	mil/yr	
1	38.0000	10.7798	7.50001

Notice that the corrosion rate has decreased from 27.9 to 10.8 mil/year, a decreased of around 60%. The pH is 7.5 - the target pH. Based on these results neutralizing the pH had a partial effect on corrosion reduction. A different mitigation strategy can be studied, for example changing the alloy.

### Changing the Alloy

In this section different alloys will be tested under the same environmental conditions, i.e., at a pH=3.9 and 38°C.

#### 13%Cr Stainless Steel

1. Under the **Gas Saturated with Water** stream, add a new **Corrosion Rate** single point calculation.
2. Change the name to **13Cr Alloy** using the **<F2>** key
3. Change **Flow Type** to **Pipe Flow** (Leave the default values of pipe diameter= 10 cm and pipe flow velocity of 2 m/s)
4. **Change** the **contact surface** to **13%Cr stainless steel**

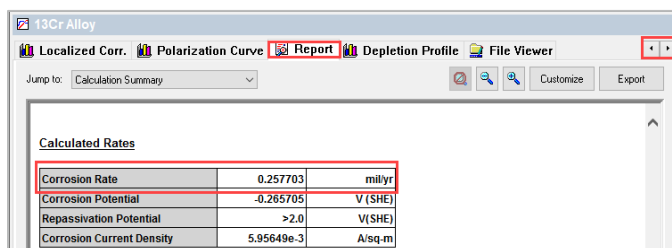
Your screen should look like the image below.

Calculation Parameters	
Calculation Type	Isothermal
Flow Type	Pipe Flow
Pipe Diameter (cm)	10.0000
Pipe Flow Velocity (m/s)	2.00000
Thermal Aging Temperature (°C)	399.000
Thermal Aging Time (hr)	0.0
Inflows (mole %)	
H2O	5.54202
CO2	77.3001
N2	0.0199742
H2S	16.5786
CH4	0.499355
C2H6	0.0299613
C3H8	0.0299613
H2	5.14186e-25
O2	2.57093e-25
Fe	0.0
Contact Surface	
Fe(86.850)Cr(13.000)C(0.150)	

- 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

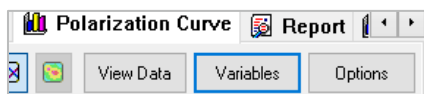
- Click on the **Report** tab to see the results. (You may need to use the ◀▶ buttons to move the tabs and find the Report tab).
- Go to the **Calculated Rates** table



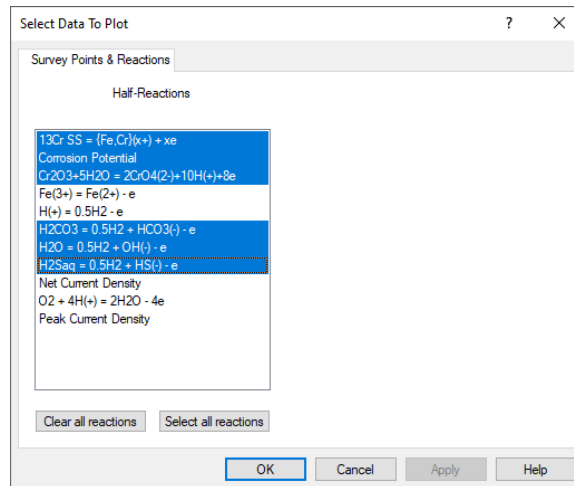
Calculated Rates		
Corrosion Rate	0.257703	mil/yr
Corrosion Potential	-0.265705	V (SHE)
Repassivation Potential	>2.0	V(SHE)
Corrosion Current Density	5.95649e-3	A/sq.m

The corrosion rate of 13%Cr is one order of magnitude lower when compared to the corrosion rate for Carbon Steel, i.e. at 0.25 mil/yr for 13%Cr vs 27.9 mil/yr for Carbon Steel. This is consistent with the use of 13% Cr to protect against CO<sub>2</sub> corrosion.

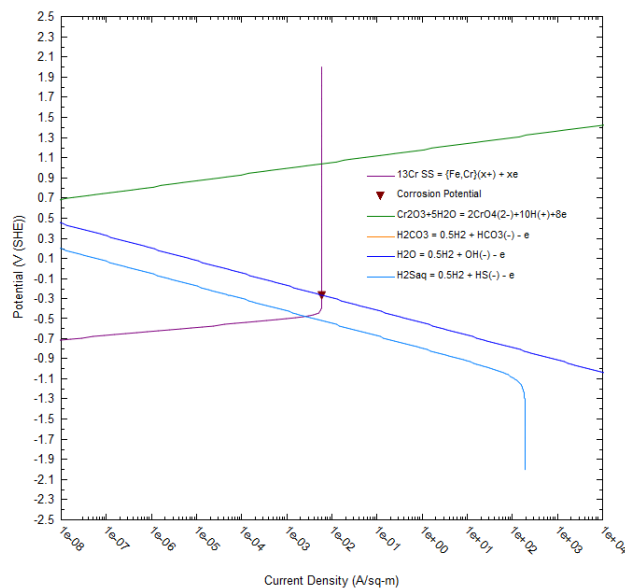
- Click on the **Polarization Curve** tab (  Polarization Curve ).
- Let's modify the plot to make it easy to interpret. Click on the **Variables** button. This will open a new window.



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



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



Modified polarization curve showing the main anodic and cathodic reactions contributing to the corrosion process.

The anodic reaction is represented by the **purple line**. The main cathodic reactions contributing to the total corrosion process are the water reduction reaction (**blue line**) and the reduction reaction of  $\text{H}_2\text{S}_{\text{aq}}$  to  $\text{HS}^-$  (**light blue line**) in a lesser degree.

The corrosion potential (represented by the red triangle) of 13%Cr is -0.266 V vs SHE and the corresponding corrosion current  $i_{\text{corr}}=5.95\text{e-}3 \text{ A/m}^2$ . The  $i_{\text{corr}}$  for Carbon Steel was  $0.61 \text{ A/m}^2$ , this means that 13%Cr is approximately 100x more resistant to corrosion under the same conditions.

Stainless Steel 304

- ✓ Copy **13Cr Alloy** corrosion calculation, and **paste** it under the stream 'Saturating Gas with Water'
- ✓ Change the name to **304SS** using the <F2> key
- ✓ **Change** the **contact surface** to **Stainless Steel 304**
- ✓ Make sure everything else remain the same (since we are simulating the same operating conditions)

Your screen should look like the image below.

Calculation Parameters	
Calculation Type	Isothermal
Flow Type	Pipe Flow
Pipe Diameter (cm)	10.0000
Pipe Flow Velocity (m/s)	2.00000
Thermal Aging Temperature (°C)	399.000
Thermal Aging Time (hr)	0.0
Inflows (mole %)	
H2O	5.54202
CO2	77.3001
N2	0.0199742
H2S	16.5786
CH4	0.499355
C2H6	0.0299613
C3H8	0.0299613
H2	5.14186e-25
O2	2.57093e-25
Contact Surface	
Fe(86.850)Cr(13.000)C(0.150)	

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

#### 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	0.141686	mil/yr
Corrosion Potential	-0.172912	V (SHE)
Repassivation Potential	>2.0	V(SHE)
Corrosion Current Density	3.32060e-3	A/sq-m

The corrosion rate of 304 SS is now 0.14 mil/year. The corrosion rate of 13%Cr is 0.25 mil/yr and the corrosion rate for Carbon Steel is 27.9 mil/yr. Based on these results, the order of corrosion resistance for the same environment is 304SS > 13%Cr > Carbon Steel

- ✓ 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**.

Select Data To Plot

Survey Points & Reactions

Half-Reactions

2H2O = O2 + 4H(+) + 4e

Corrosion Potential

Fe(3+) = Fe(2+) - e

H(+) = 0.5H2 - e

H2CO3 = 0.5H2 + HCO3(-) - e

H2O = 0.5H2 + OH(-) - e

H2Saq = 0.5H2 + HS(-) - e

Net Current Density

O2 + 4H(+) = 2H2O - 4e

Peak Current Density

S30400 = (Fe,Cr,Ni)(x+) + xe

Clear all reactions

Select all reactions

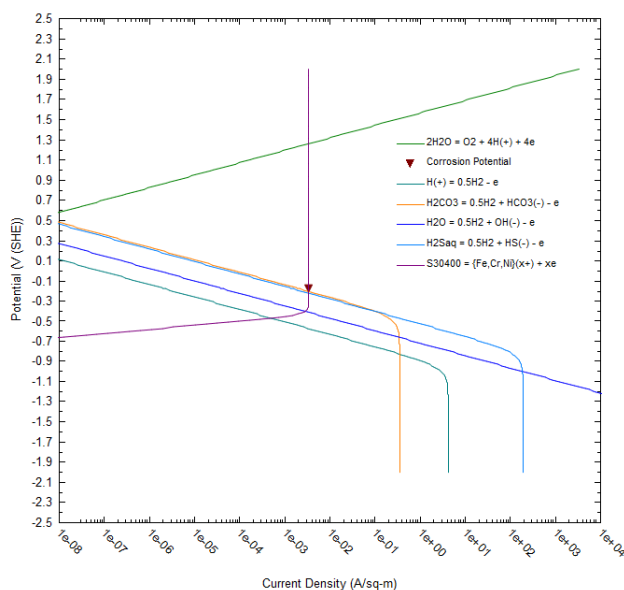
OK

Cancel

Apply

Help

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



Modified polarization curve showing the main anodic and cathodic reactions contributing to the corrosion process.

The anodic reaction is represented by the **purple line**. The main cathodic reactions contributing to the total corrosion process are the reduction reaction of  $\text{H}_2\text{CO}_3$  to  $\text{HCO}_3^-$  (**orange line**) and the reduction reaction of  $\text{H}_2\text{S}_{\text{aq}}$  to  $\text{HS}^-$  (**light blue line**). The water reduction reaction (**blue line**) and the  $\text{H}^+$  reduction reaction (**turquoise line**) contribute to the corrosion process in a lesser degree.

The corrosion potential of SS304 is -0.17 V vs SHE and the corresponding corrosion current  $i_{\text{corr}} = 3.3 \times 10^{-3} \text{ A/m}^2$ . 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

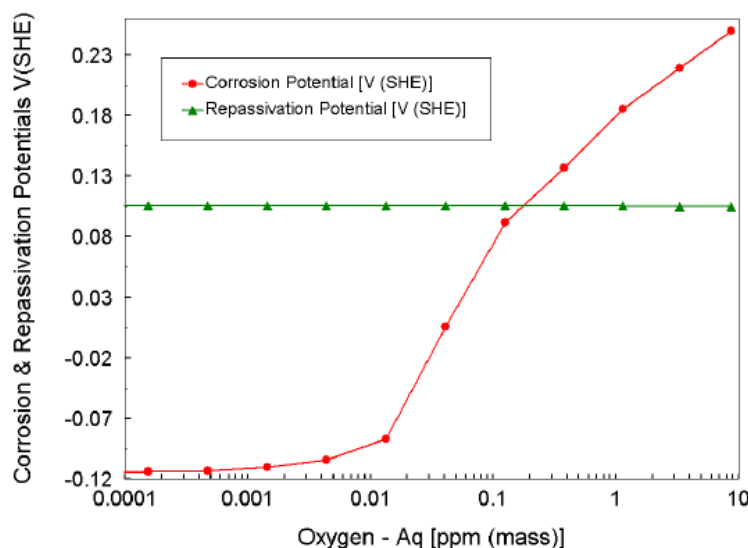
The OLI Studio: Corrosion Analyzer, includes the ability to predict the repassivation potential ( $E_{rp}$ ) and a peak current density for active pits. The repassivation potential is important for corrosion analysis because it indicates how well an alloy can “repassivate” active pits. Additionally, 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. When  $E_{corr} > E_{rp}$  the alloy becomes susceptible to localized corrosion. The wider the  $E_{corr} - E_{rp}$  difference, the greater the propensity for localized corrosion

### 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 stainless steel 316. 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.

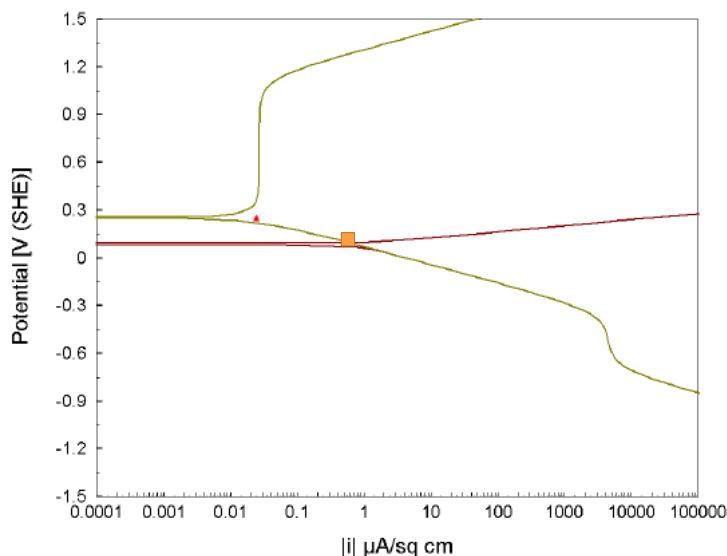


Repassivation and Corrosion Potential for 316 stainless steel in brackish water at various levels or aeration.

## Peak Current Density

The peak current is defined by OLI as the current density in the most active pit<sup>2</sup>. 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.

The figure below, shows the peak current (red curve) for active pits superimposed on the general corrosion polarization curve (yellow curve). The stopping current density repassivation criterion is  $0.01 \text{ A/m}^2$ .



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.

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<sup>2</sup> maximum propagation rate of an isolated pit

# General Corrosion Rate and Propensity to Localized Corrosion

## Corrosion Rate Survey Calculations

### Corrosion Rate of SS 304 as a function of temperature (single survey)

Within the corrosion analyzer tool, the effect of different variables such as T, P, pH, etc. on corrosion rates can be analyzed.

In this example, we are going to learn how to study the effect of temperature on the corrosion rate of SS-304.

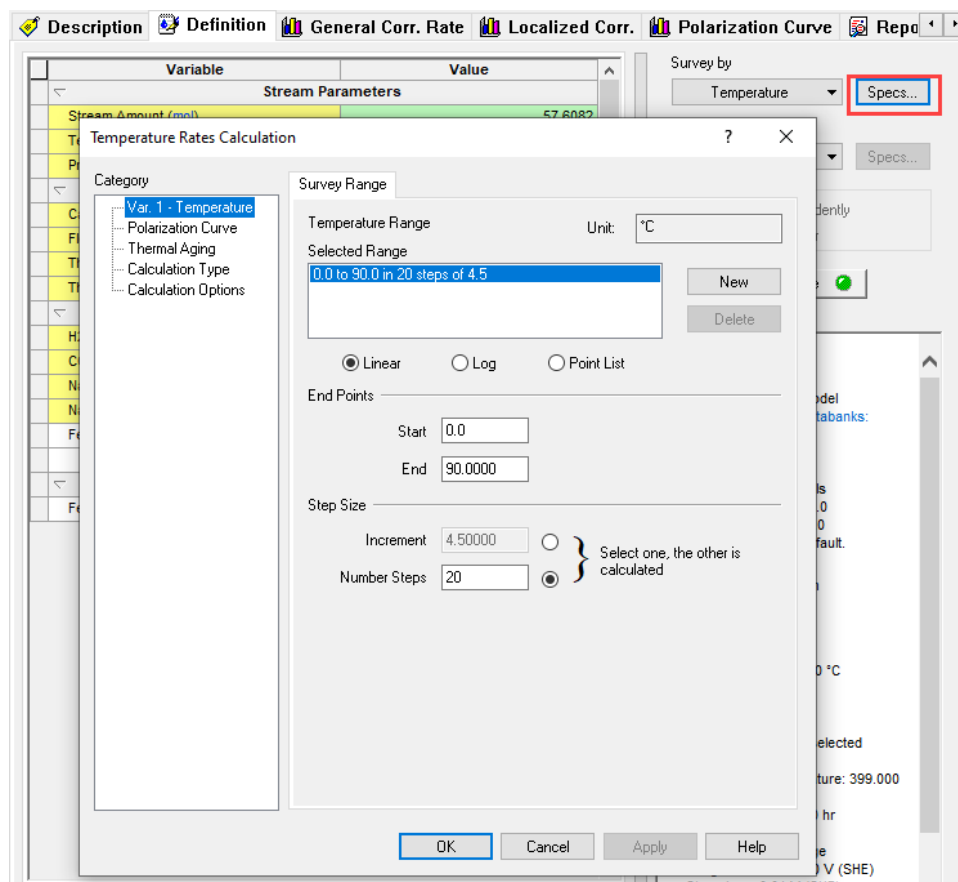
#### Starting the Simulation

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 – Survey by Temperature			
Calculation Settings		Stream Composition and Conditions	
Stream Name	Corrosion Rate Surveys	Stream Amount	Calculated
Name Style	Display Formula	Temperature	0-90°C
Unit Set	Metric, Batch, Moles	Pressure	1 atm
Framework	AQ	H2O	55.5082 moles
Calculation Type	Corrosion Rates	CO2	1 mole
Contact Surface	Stainless Steel 304	NaHCO3	0.1 moles
		NaCl	1 mole

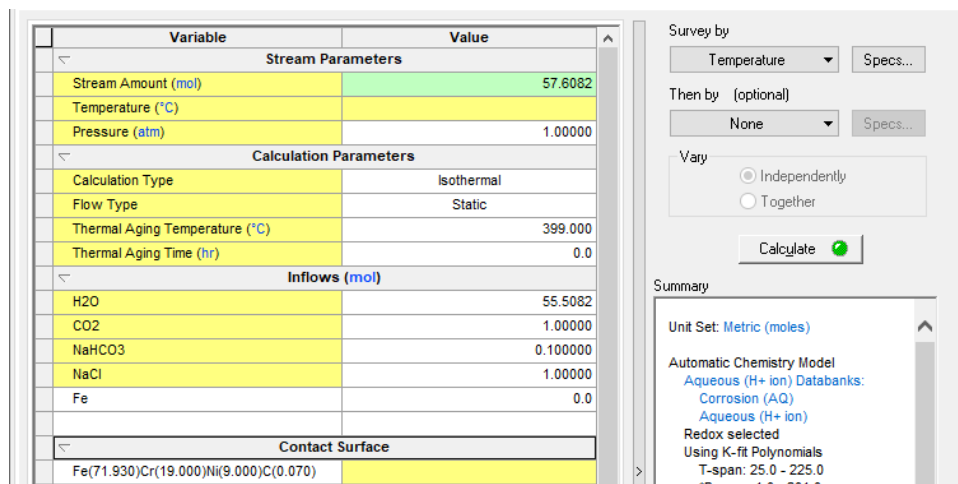
- ✓ Add a new **Stream**
- ✓ **Click** on the new Stream and press **<F2>** to change the name to **Corrosion Rate Surveys**
- ✓ Select the **AQ** thermodynamic Framework
- ✓ **Click** on the **Names Manager** Icon and select the **Formula** option
- ✓ **Click** on the **Units Manager** Icon, and select Metric, Batch, Moles
- ✓ Enter the composition and pressure of the stream given in the table above
- ✓ Go to the **Add Calculation** button and select **Corrosion Rates** calculation
- ✓ Rename the corrosion rate calculation as **CR vs T - 304SS**
- ✓ **Go** to the **Survey by** option and select **Temperature**. This option will allow you to calculate the corrosion rate at a specified temperature range.
- ✓ Click on the **Specs...** button to define the temperature range
  - Temperature range: 0 – 90 °C
  - Number of steps: 20
- ✓ Click **OK** to accept the changes
- ✓ Select **Static** as they Type of Flow






- ✓ Select alloy **Stainless Steel 304** as the contact surface

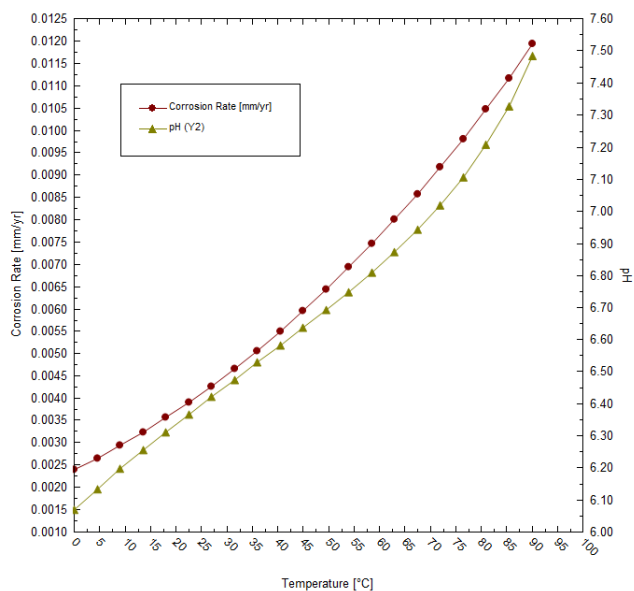
Your screen should look like the image below



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

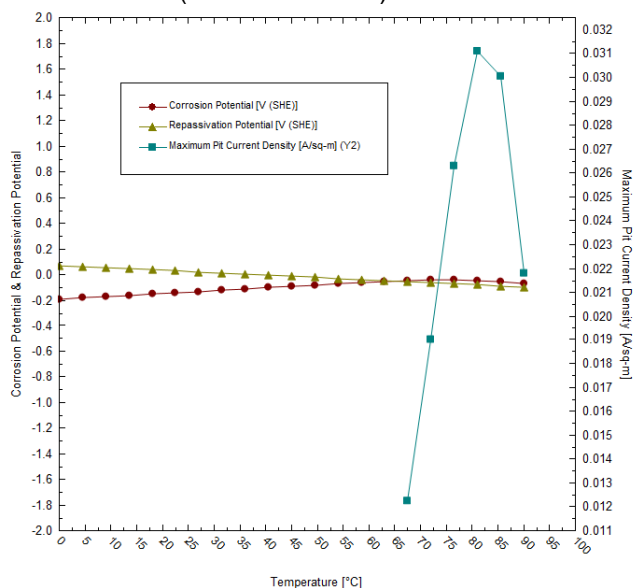
## Analyzing the Results

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



The predicted corrosion rate increases as a function of T, as well as the pH value. These results show that SS304 have very low corrosion rates even if we increase the temperature up to 90°C. So, in theory this alloy would be suitable for service at different temperatures. However, is this alloy susceptible to localized corrosion? That's what we need to find out next.

- ✓ Click on the **Localized Corr. Rate** tab (  **Localized Corr.** )



This tab displays a plot showing the results of three different calculated data:


- Corrosion Potential,  $E_{corr}$  (red dotted line)
- Repassivation Potential,  $E_{rp}$  (yellow triangle line)

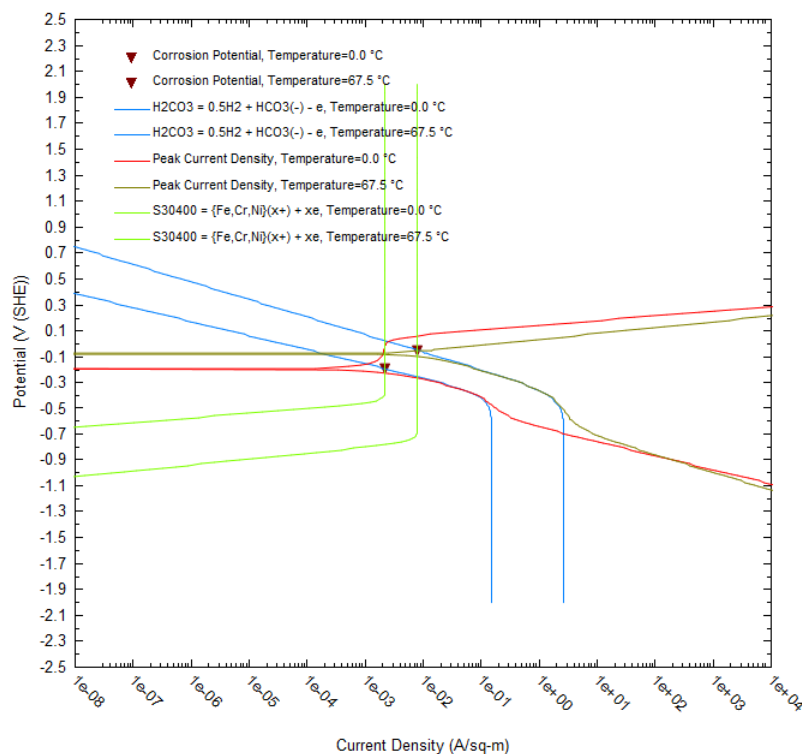
- Maximum Pit Current Density (blue square line)


The  $E_{rp}$  can be compared to the  $E_{corr}$  in the same environment to determine the alloy's susceptibility to localized corrosion. When  $E_{corr} > E_{rp}$  the alloy becomes susceptible to localized corrosion. The wider the  $E_{corr} - E_{rp}$  difference, the greater the propensity for localized corrosion.

In this example, at a  $T > 67^\circ\text{C}$  the  $E_{corr} > E_{rp}$  and localized corrosion is predicted to occur. The blue squares indicate the magnitude of the worst pitting scenario at each temperature.

The effect of temperature can be studied using the polarization curves.

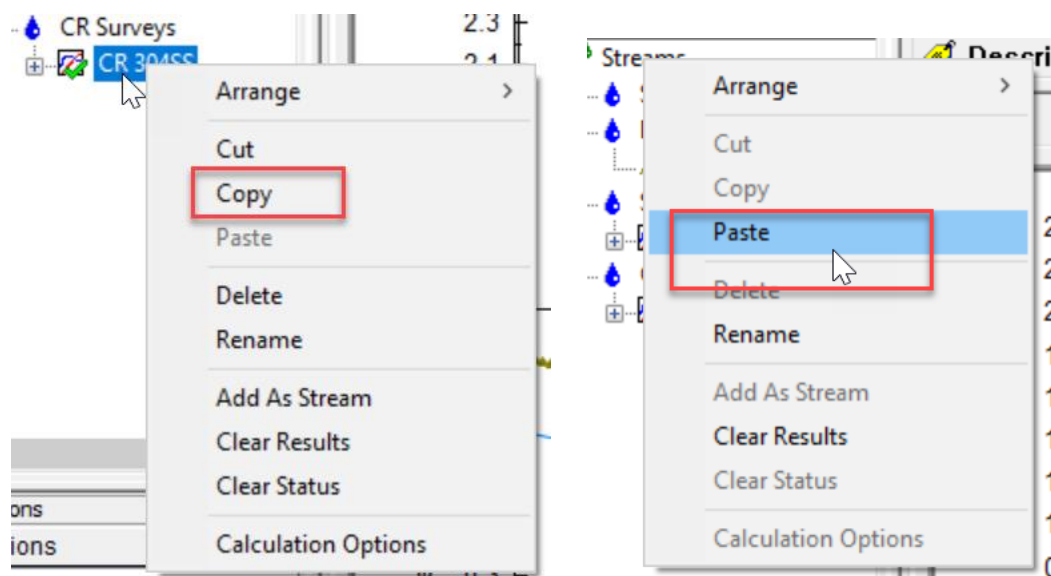
- ✓ Click on the **Polarization Curve** tab (  **Polarization Curve** ). This tab displays a plot showing the calculated polarization curve of stainless steel 304.
- ✓ Modify the plot (in the **variables** button) such that the anodic reaction, the carbonic acid reduction reaction, the corrosion potential, and the peak current density are the only values shown.



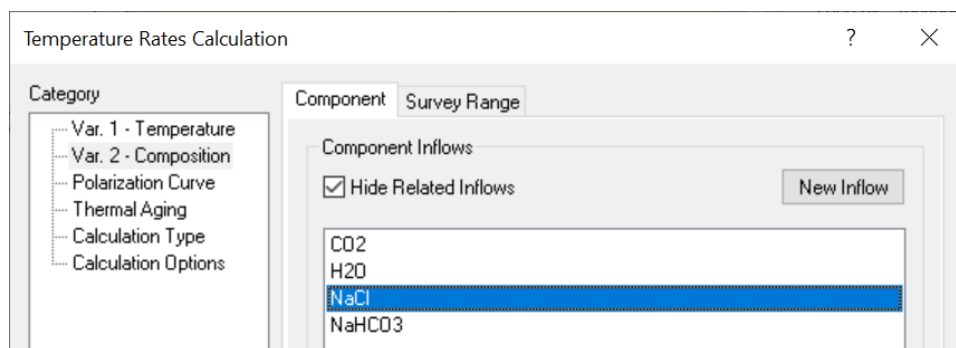
After modifying the polarization curve, we can see the effect of temperature in both the anodic dissolution of stainless steel 304 (green curves) and the main cathodic reaction (the reduction of H<sub>2</sub>CO<sub>3</sub>) (light blue curves); both reactions increase in magnitude as the temperature increase, which has a direct impact on the corrosion potential as well. However, notice that for the 0°C case, the peak current density (red curve) cuts the anodic curve at a higher potential (this is the repassivation potential) compared to the corrosion potential, i.e.,  $E_{rp} > E_{corr}$ . This is the reason why localized corrosion is not predicted at this temperature. In the 67.5°C case, the peak current density (yellow curve) cuts the anodic curve at lower potential compared to the corrosion potential, i.e.,  $E_{corr} > E_{rp}$ , and localized corrosion is predicted to occur. The difference between these two values ( $E_{corr}$  and  $E_{rp}$ ) is small and cannot be seen easily in the plot, you need to zoom in .

## Corrosion Rate of SS 304 as a function of temperature and NaCl concentration (dual survey)

- ✓ **Copy** and then **paste** the **CR 304SS** single point rate to create a new survey calculation



- ✓ Rename the new survey calculation as **CR 304SS (T, NaCl)**
- ✓ Go to the **Survey by** option and select **Temperature** then by **Composition**. This option will allow you to calculate the corrosion rate at a specified temperature and NaCl concentration range.
- ✓ Click on the **specs...** button next to the composition option. This opens a new window.
- ✓ Under the **component** tab select NaCl



- ✓ Under the **Survey Range** tab enter the following range:
  - Range: 0- 5.5. moles
  - Number of steps: 20

Temperature Rates Calculation

Category

- Var. 1 - Temperature
- Var. 2 - Composition
- Polarization Curve
- Thermal Aging
- Calculation Type
- Calculation Options

Component Survey Range

Composition Range Unit: mol

Selected Range

0.0 to 5.5 in 20 steps of 0.275

New

Delete

☒ Linear ☐ Log ☐ Point List

End Points

Start 0.0

End 5.50000

Step Size


Increment 0.275000 ☐ } Select one, the other is calculated

Number Steps 20 ☒

OK Cancel Apply Help

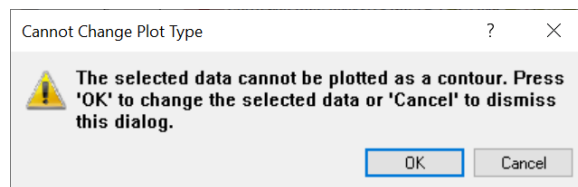
- ✓ Click OK
- ✓ Click **Calculate**

## Analyzing the Results

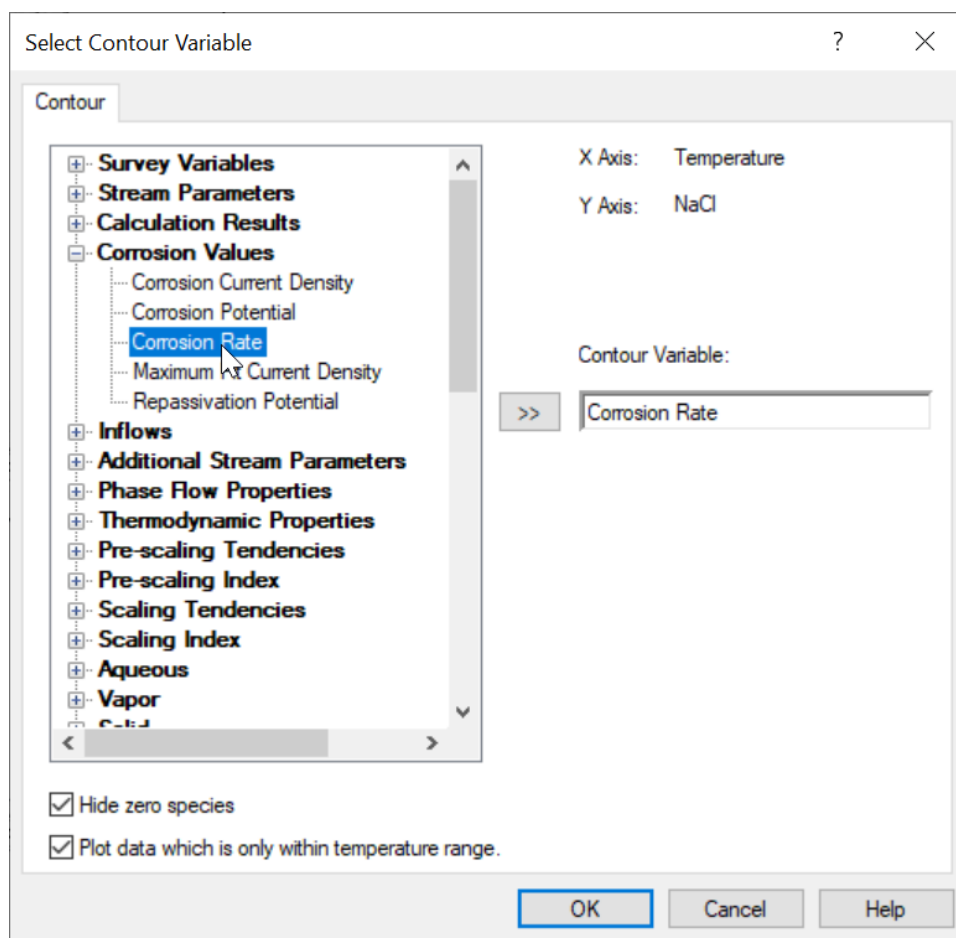
- ✓ Click on the **General Corr. Rate** tab (  General Corr. Rate ). This tab displays a plot showing the results of corrosion rate and pH as a function of temperature and concentration.

This plot is too hard to read. Fortunately we have the option of creating a contour plot to visualize the results in a much better way.

- ✓ Click on the **Contour Plot** icon . An error message will appear. Click OK



- ✓ A new window appears asking you to select the contour variable of interest. Go to the **corrosion values** category and expand it. Select **Corrosion rate** by double clicking on it.



- ✓ Click OK

## Entering Ionic Inputs - 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

Description		Analysis		Report	
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			

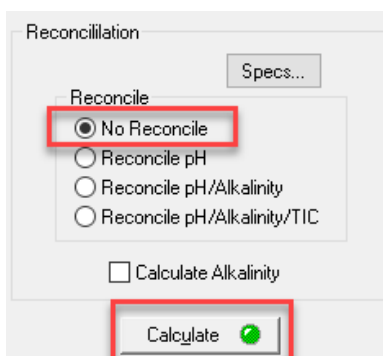
Add Reconciliation


Template Manager  
Standard  
Save as...

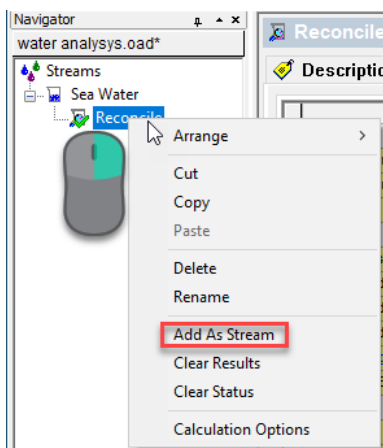
Summary  
Unit Set: Metric (mass concentration)  
Automatic Chemistry Model  
Aqueous (H+ ion) Databanks:  
Aqueous (H+ ion)  
Using K-ft Polynomials  
T-span: 25.0 - 225.0  
P-span: 1.0 - 1500.0

- ✓ Click on the **Add Reconciliation** button

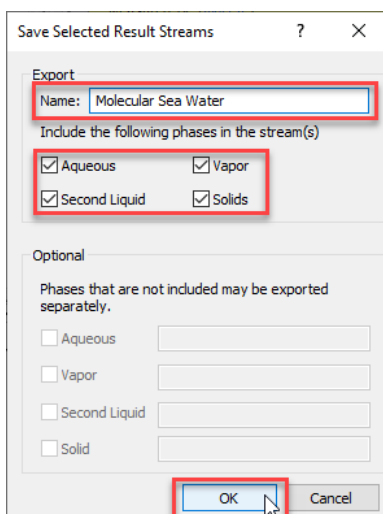
- ✓ Select the **No reconcile** option and click on the **calculate** button



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

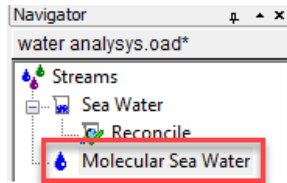


- ✓ A new window opens. Change the name to **Molecular Sea Water**, leave the default selections and click **OK**



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 [v]

**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.

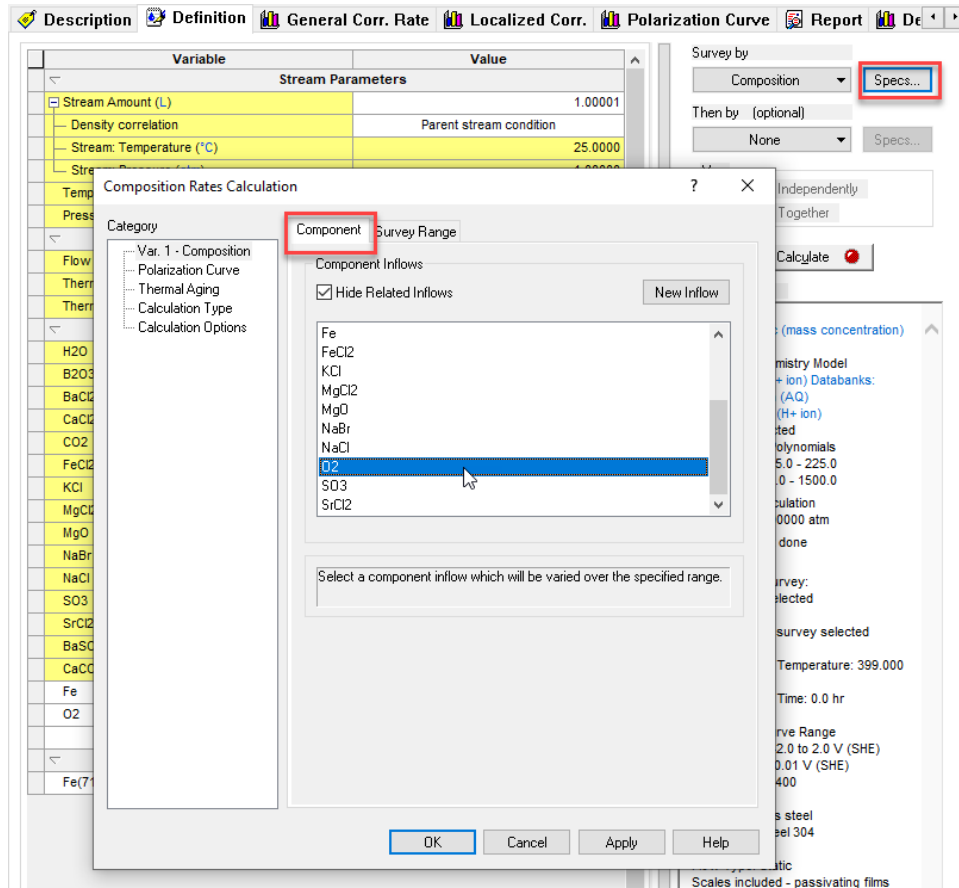
Component not selected for composition survey variable.

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.

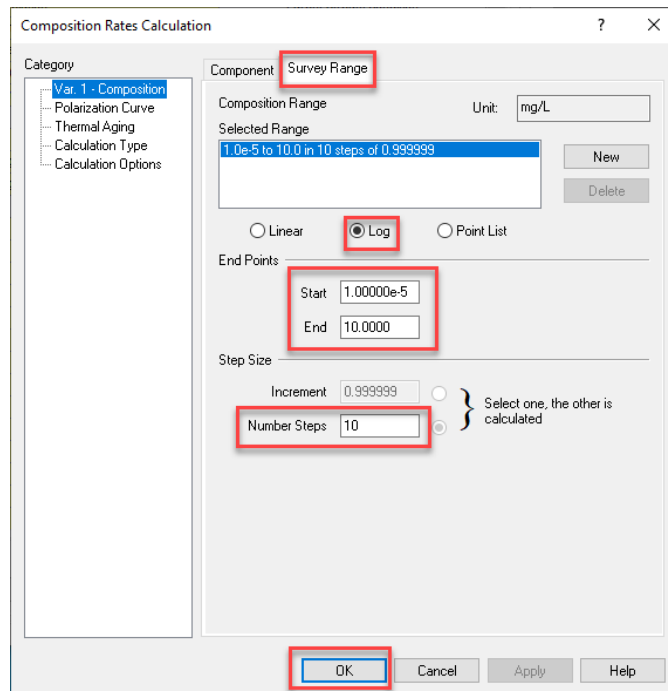
- ✓ Under **Inflows** type O2

Inflows (mg/L)	
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

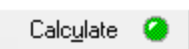
- ✓ Click on the **Specs** button (as shown in the image below). This will open a new window. **Select O2** as the component to vary



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



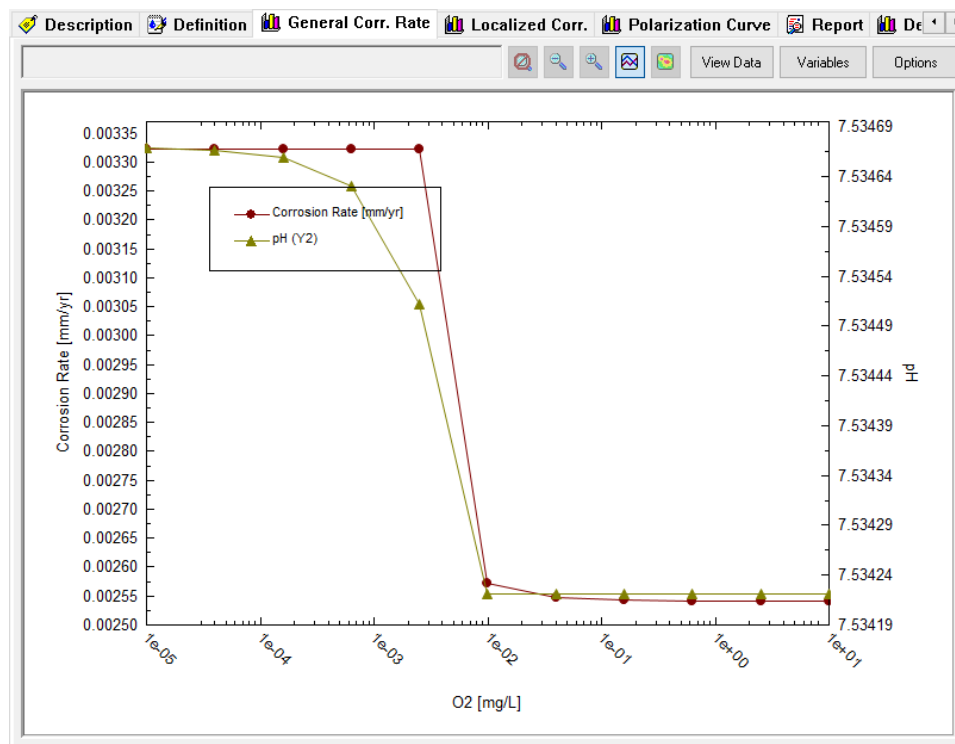
- ✓ Click the **Calculate** button



## Analyzing the Results

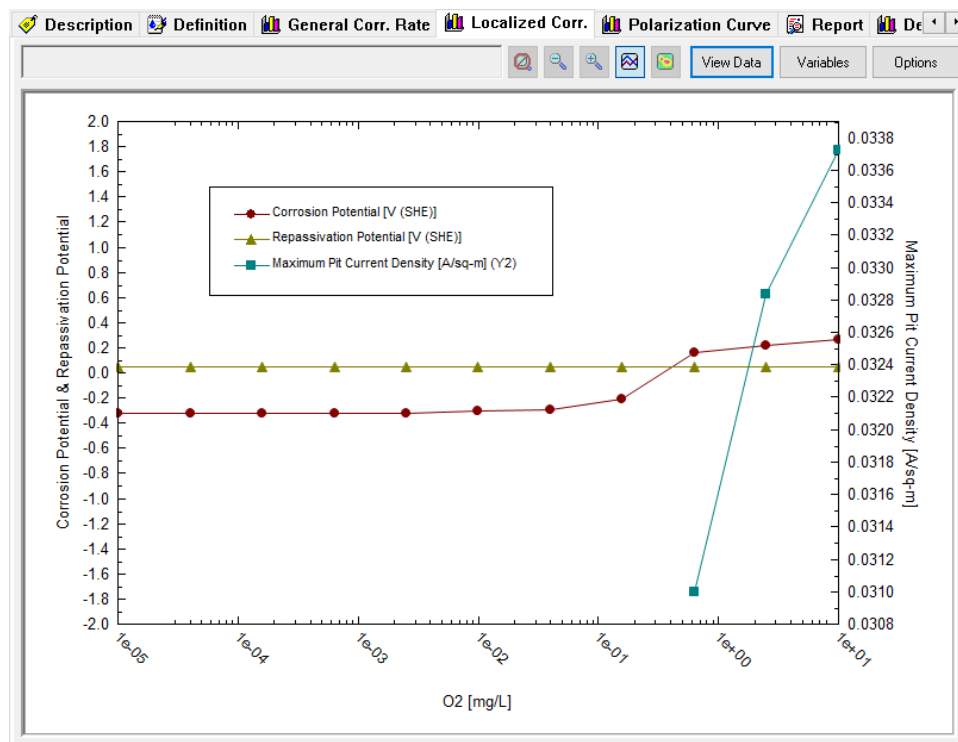
- ✓ Go to the **General Corr. Rate** tab

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

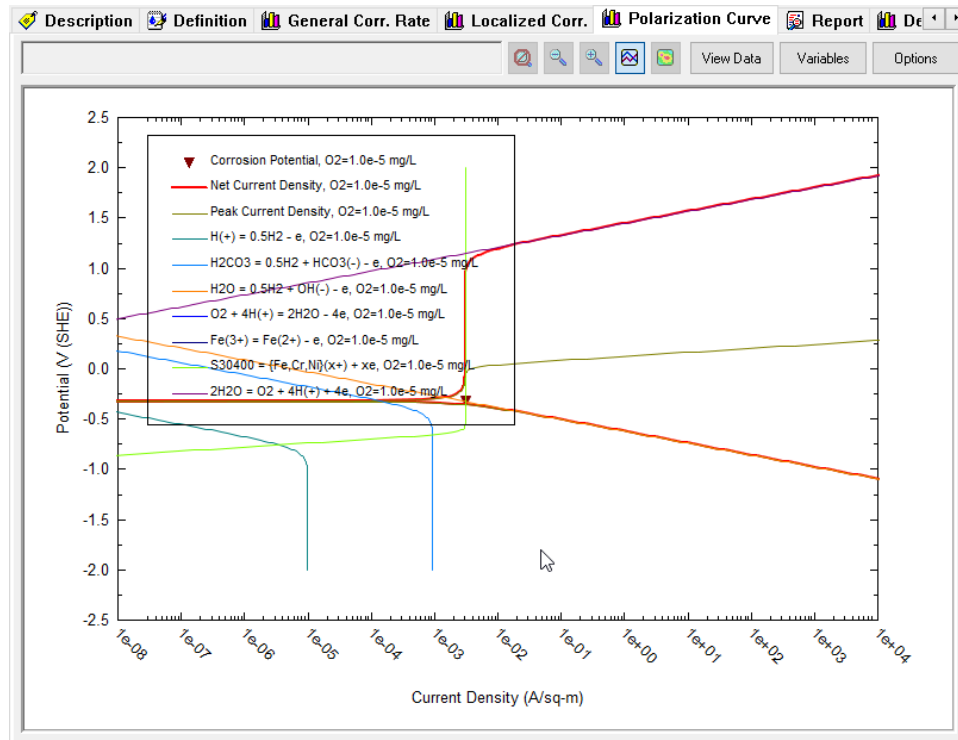


Notice that the software is predicting pitting corrosion at oxygen concentrations above 0.6 mg/L. The reason for the failure of SS304 in sea water has to do with the susceptibility of the passive film to be attacked/damaged by chlorides. The software is predicting the possible failure of type 304 by 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.

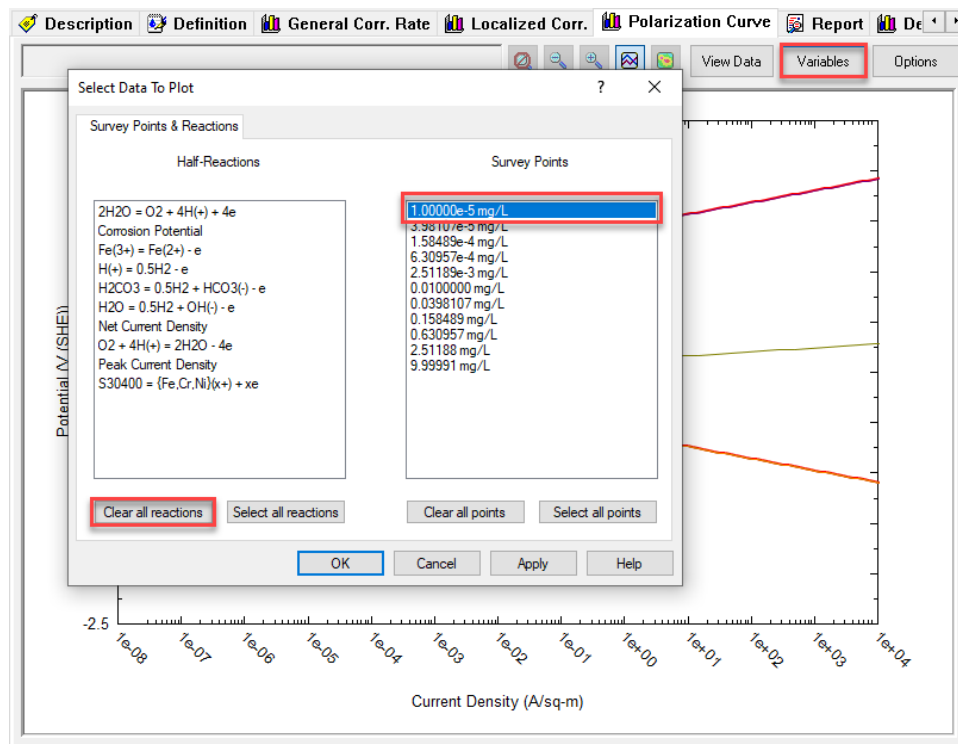
Why is the corrosion potential increases above a 0.6 mg/L of oxygen content, hence increasing the susceptibility to localized corrosion? To further understand this, we can go to the **Polarization Curve** tab.

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

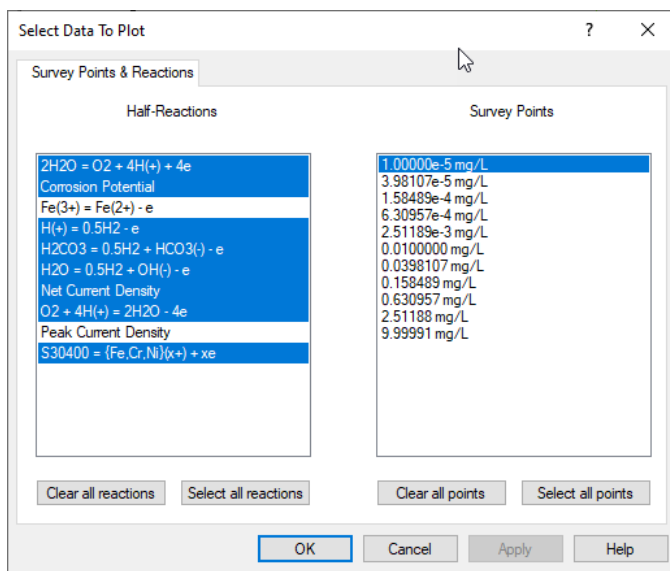


You will find a default plot shows both the net polarization curve (in red) and the half-reactions that contribute to the net polarization curve.

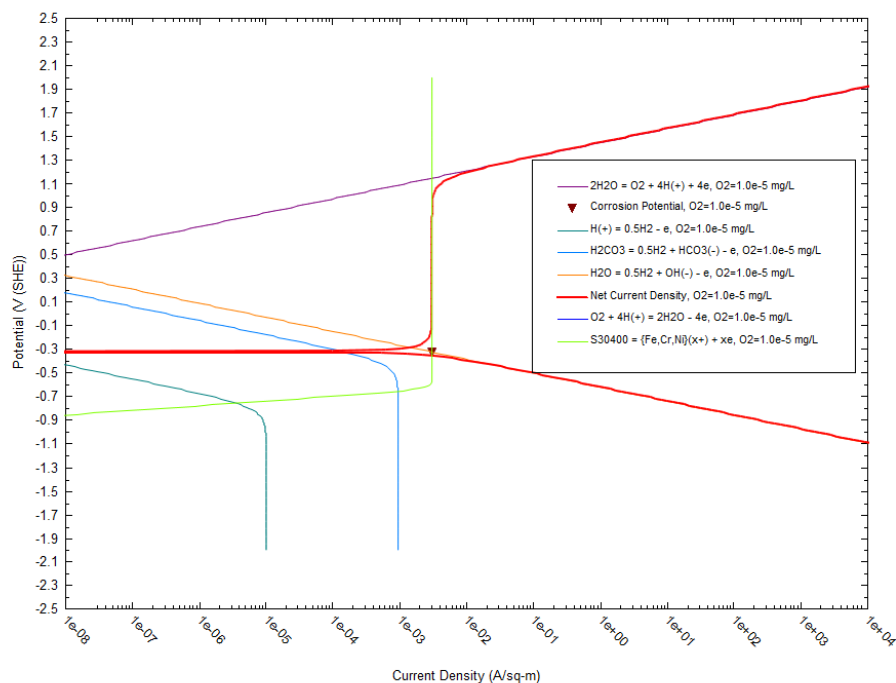
- ✓ Click on the **variables** button. This will open a new window



- ✓ 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.

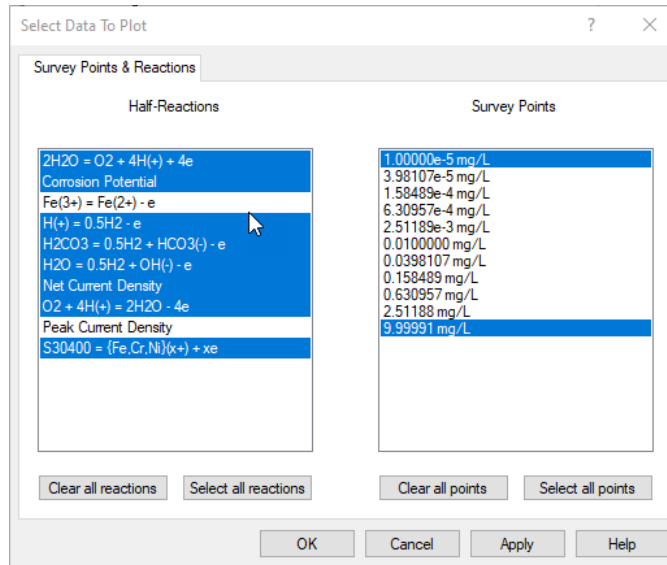


The polarization curve should look like the image below

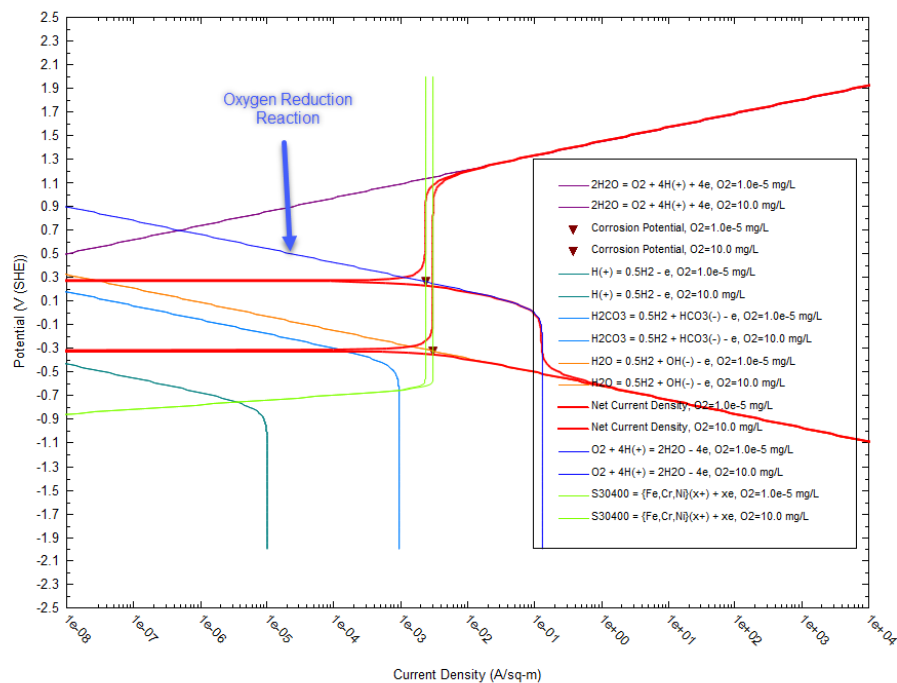


Notice that the corrosion potential (located at the red triangle) is -0.32 V vs SHE, and that the oxygen reduction reaction ( $\text{O}_2 + 4\text{H}(+) = 2\text{H}_2\text{O} - 4\text{e}$ ) is not contributing to the net current density.

- ✓ 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.



## Chapter V – Corrosion Prediction in Upstream Oil and Gas Using

### O<sub>2</sub> Upsets

Calculate **corrosion rate** on **carbon steel, 316** and **2205** in a range of temperature (50-120 °C) on a liquid full water stream, where gas blanketing upset (N<sub>2</sub>) has been experienced in degasser.

Nominal N<sub>2</sub> spec is 99.9% purity (0.01% O<sub>2</sub>), but upsets to 98% or 95% (5% O<sub>2</sub>) can be experienced.

1 atm at pump suction and 100 atm at pump discharge.

For this example, we are going to use the file named **Khuff Reservoir.oad** and are going to use the water analysis named **Well H1 (as received at plant)**.

#### Calculating Corrosion Rates for Carbon Steel

- ✓ **Select** the **Well H1 (as received at plant)**, right click on it and select **Add as Stream**
- ✓ **Leave** the default name and include all the phases, then Click **OK**. This creates a new stream.
- ✓ Change the Thermodynamic Framework of the new stream to **AQ**
- ✓ Change the pressure to 100 atm (this will simulate the discharge pressure) and Temperature to 65 °C.
- ✓ In the new exported stream, change the units from **concentration** (e.g., mg/L) to **Metric | Batch | Mass Fraction**
- ✓ Change units of **mass fraction** from **mass%** to **ppm (mass)**
- ✓ Add **O2** in the inflows
- ✓ Leave **carbon steel G10100 (Generic)** as the **contact surface**
- ✓ **Add a Corrosion Rate** calculation and rename it **Carbon Steel / O2**
- ✓ Go to the **Survey by** option and select **Composition** and then by **Temperature**
- ✓ Click on the **specs...** button next to the composition button. This opens a new window.
  - a. Select the Composition Survey
  - O2: 1-e3 – 8 ppm ; 20 steps; log scale

Composition Rates Calculation

Category

- Var. 1 - Composition
- Var. 2 - Temperature
- Polarization Curve
- Calculation Type
- Calculation Options

Component Survey Range

Composition Range Unit: ppm (mass)

Selected Range

1.0e-3 to 8.0 in 20 steps of 0.39995

New

Delete

☐ Linear ☒ Log ☐ Point List

End Points

Start 1.00000e-3

End 8.00000

Step Size

Increment 0.399950 ☐ } Select one, the other is calculated

Number Steps 20 ☒

- b. Select the Temperature Survey
- Temperature range: 50 – 120 C ; 20 steps

Composition Rates Calculation

Category

- Var. 1 - Composition
- Var. 2 - Temperature
- Polarization Curve
- Calculation Type
- Calculation Options

Survey Range

Temperature Range Unit: °C

Selected Range

50.0 to 120.0 in 10 steps of 7.0

New

Delete

☒ Linear ☐ Log ☐ Point List

End Points

Start 50.0000

End 120.000

Step Size



Increment 7.00000 ☐ } Select one, the other is calculated

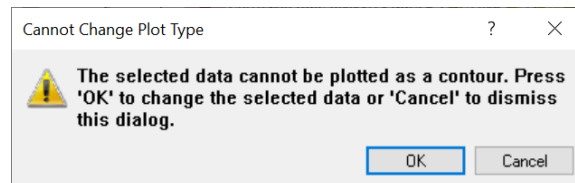
Number Steps 10 ☒

OK Cancel Apply Help

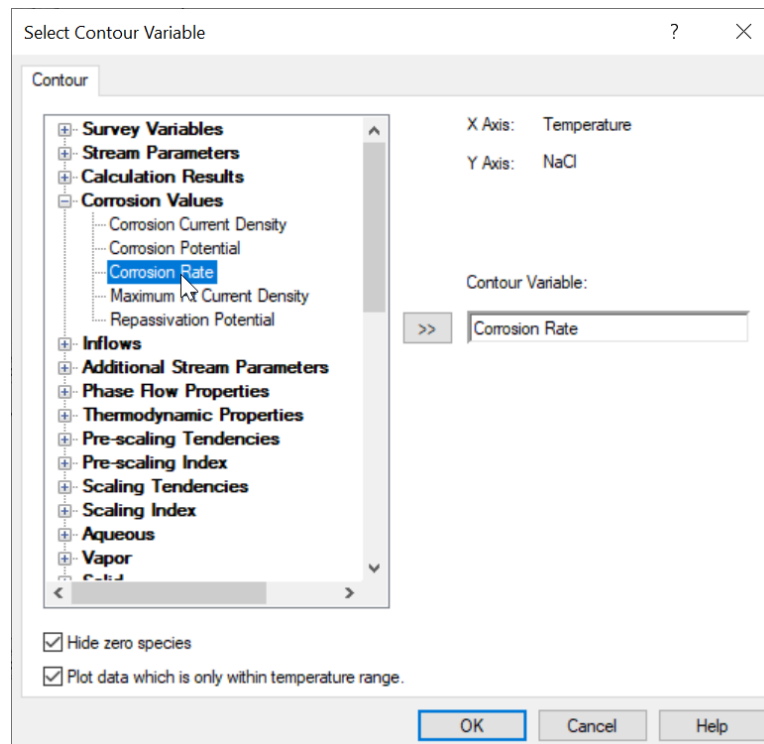
✓ Click **OK** and then **Calculate**

## Analyzing the Results

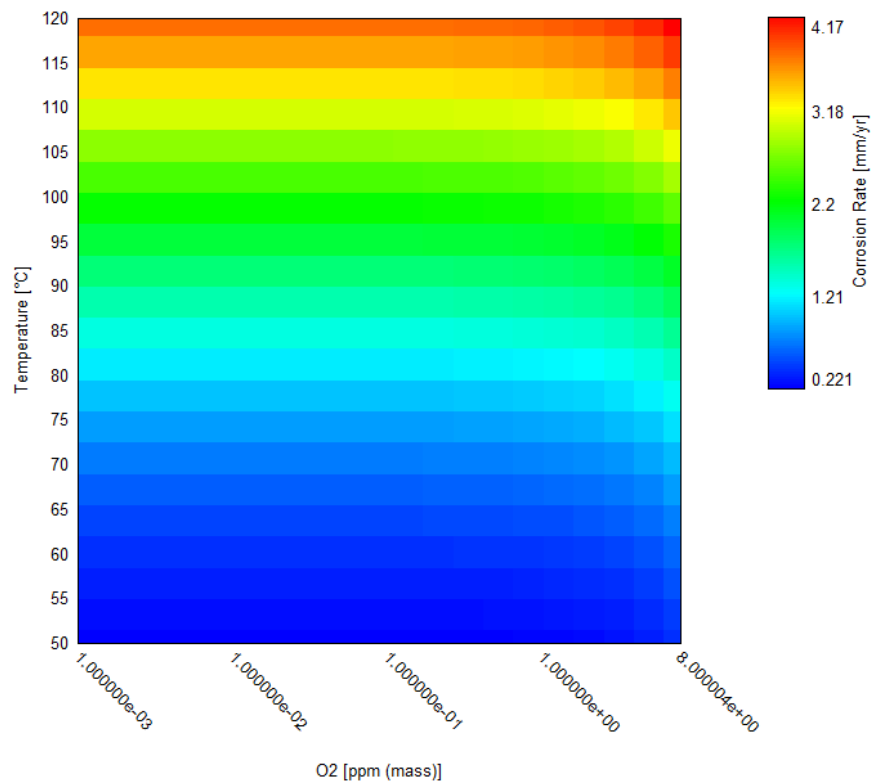
- ✓ Click on the **General Corr. Rate** tab (  **General Corr. Rate** ). This tab displays a plot showing the results of corrosion rate and pH as a function of temperature and O2 concentration.
- ✓ Click on the **Contour Plot** icon  . An error message will appear. Click OK



- ✓ A new window appears asking you to select the contour variable of interest. Go to the **corrosion values** category and expand it. Select **Corrosion rate** by double clicking on it.



- ✓ Click **OK**



This contour diagram shows the effect of both temperature and O<sub>2</sub> composition on the corrosion rate of Stainless Steel 304. The worst corrosion rate scenario occurs at the highest O<sub>2</sub> concentration and highest Temperature (top right hand side corner).

We can also calculate the corrosion rates as function of O<sub>2</sub> concentration at a single temperature = 65°C

### Calculating Corrosion Rates for Carbon Steel 1018

- ✓ Under the Exported **Well H1** stream add a **Corrosion Rate** calculation and rename it **CS vs O<sub>2</sub>**
- ✓ Go to the **Survey by** option and select **Composition**
- ✓ Click on the **specs...** button next to the composition button. This opens a new window.
  - a. Select the Composition Survey
    - O<sub>2</sub>: 1-e3 – 8 ppm ; 20 steps; log scale

Composition Rates Calculation

Category

- Var. 1 - Composition
- Var. 2 - Temperature
- Polarization Curve
- Calculation Type
- Calculation Options

Component Survey Range

Composition Range Unit: ppm (mass)

Selected Range

1.0e-3 to 8.0 in 20 steps of 0.39995

New

Delete

☐ Linear ☒ Log ☐ Point List

End Points

Start 1.00000e-3


End 8.00000

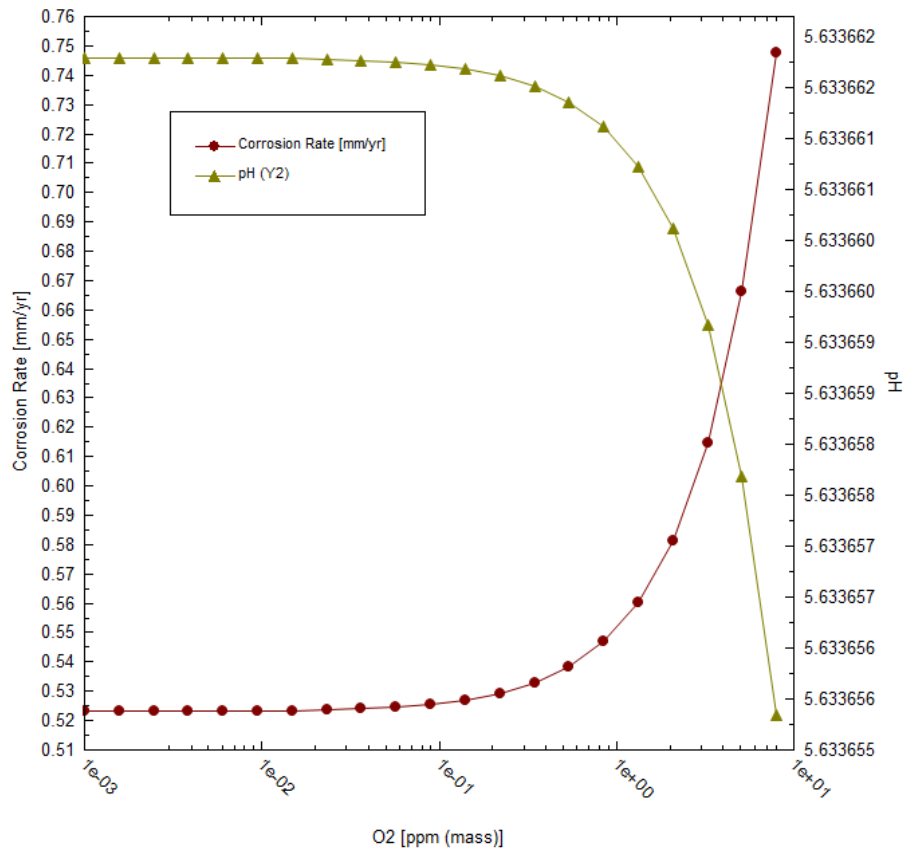
Step Size

Increment 0.399950 ☐ } Select one, the other is calculated

Number Steps 20 ☒

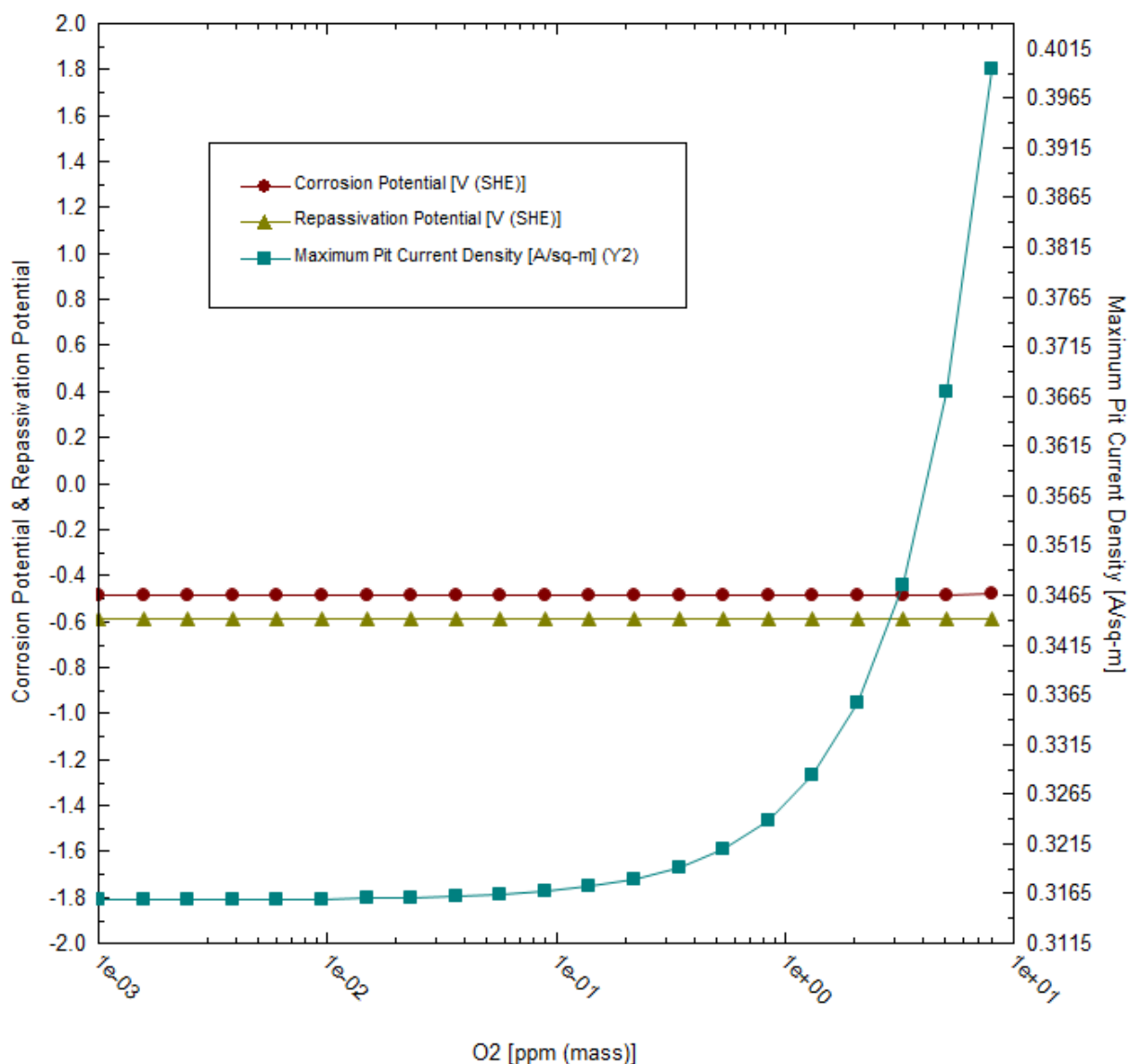
OK Cancel Apply Help

- ✓ Click **OK** and then **Calculate**
- ✓ Click on the **General Corr. Rate** tab (  **General Corr. Rate** ). This tab displays a plot showing the results of corrosion rate and pH as a function of O2 concentration.
- ✓ Right click on the X-axis and change the scale to Logarithmic scale



The corrosion rate values increase as the oxygen concentration increase. The maximum corrosion rate value is obtained at the highest O2 concentration, CR=0.75 mm/year. We can also find out if this alloy is prone to localized corrosion.

- ✓ Click on the **Localized Corr.** tab (Localized Corr. ). This tab displays a plot showing the results of corrosion potential, repassivation potential and maximum pit current density values as a function of O2 concentration.
- ✓ Right click on the X-axis and change the scale to Logarithmic scale




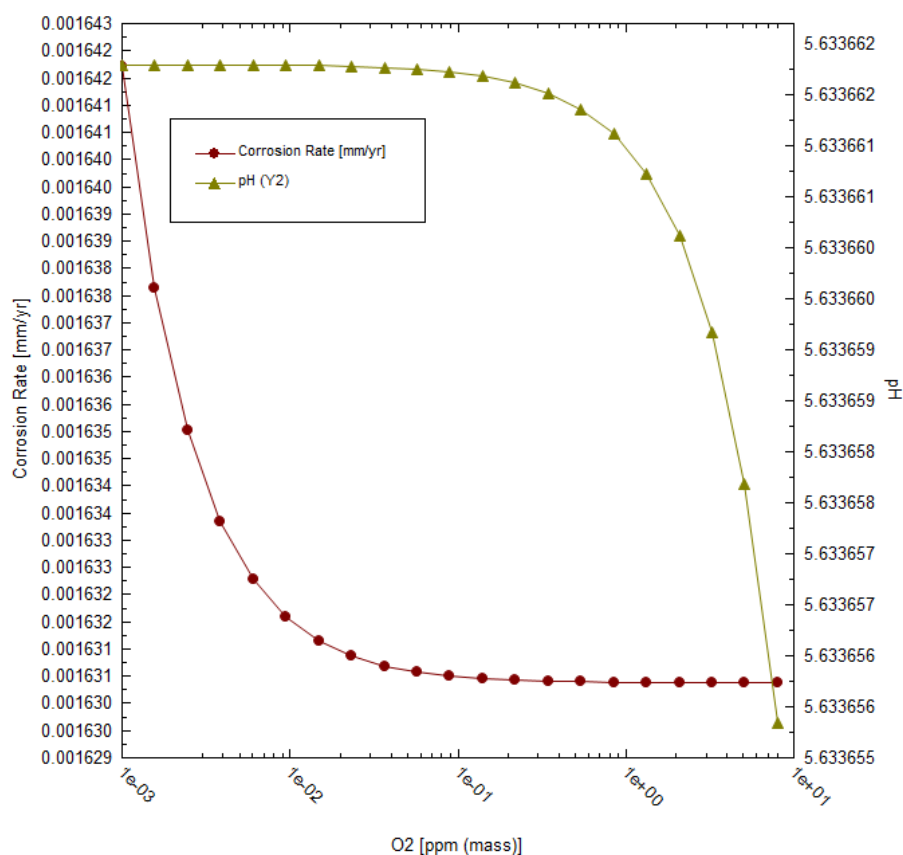
This plot shows that at all oxygen concentrations, the criterion  $E_{corr} > E_{rep}$  is met and localized corrosion is predicted to occur.

**Note:** To convert maximum pit current densities into corrosion rates is straight forward in this case because the conversion from mm/y to  $A/m^2$  units give similar values, e.g., 0.1 [ $A/m^2$ ] is roughly 0.1 mm/year.


These pitting rates are lower than the general corrosion rates and may therefore not be observable.

## Calculating Corrosion Rates for Stainless Steel 316

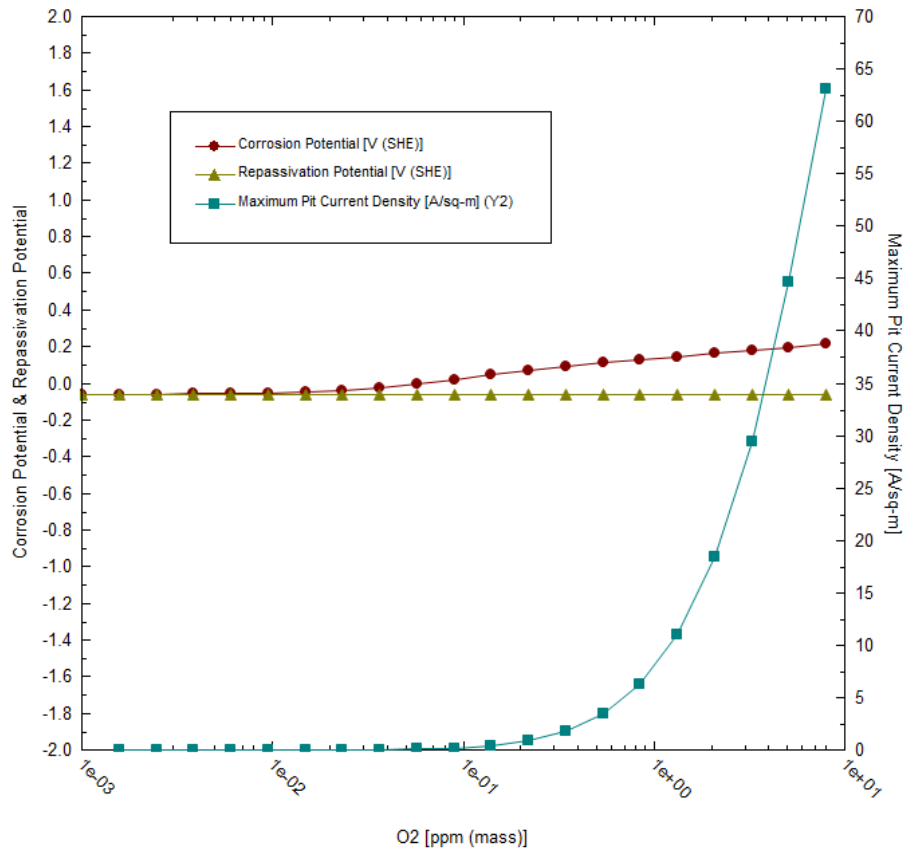
- ✓ Copy the **CS vs O2** corrosion rate calculation and then paste it on the **Molecular Well H1** stream
- ✓ Change the name to **SS 316 vs O2**
- ✓ Change the contact surface to Stainless Steel 316
- ✓ **Calculate**
- ✓ Click on the **General Corr. Rate** tab (  **General Corr. Rate** ). This tab displays a plot showing the results of corrosion rate and pH as a function of O2 concentration.
- ✓ Right click on the X-axis and change the scale to Logarithmic scale



The corrosion rate values are very small. These results suggest that the oxygen concentration is not having an impact on the general corrosion rate. But, what about the propensity to localized corrosion?


- ✓ Click on the **Localized Corr.** tab (  **Localized Corr.** ). This tab displays a plot showing the results of corrosion potential, repassivation potential and maximum pit current density values as a function of O2 concentration.
- ✓ Right click on the X-axis and change the scale to Logarithmic scale

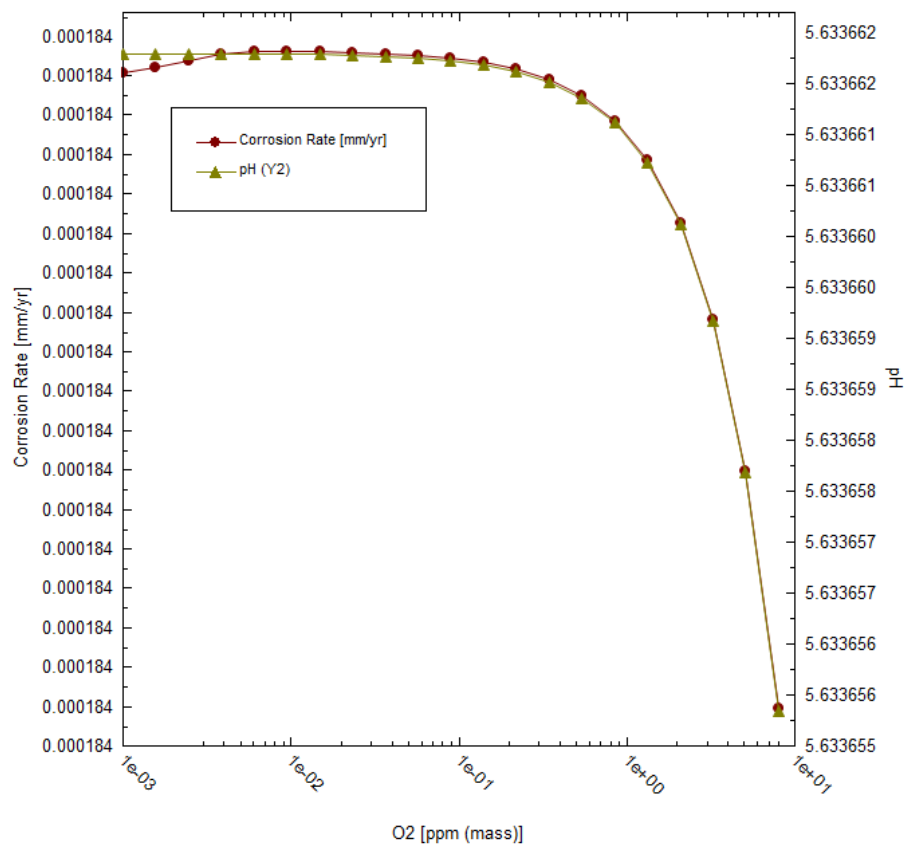




This plot shows that at concentrations higher than 0.0016 ppm of O<sub>2</sub> concentration the criterion  $E_{corr} > E_{rep}$  is met and localized corrosion is predicted to occur. Also notice that the maximum pit current density values at high oxygen concentrations are significantly higher than the predicted corrosion rates hence we will have observable pits on the surface.

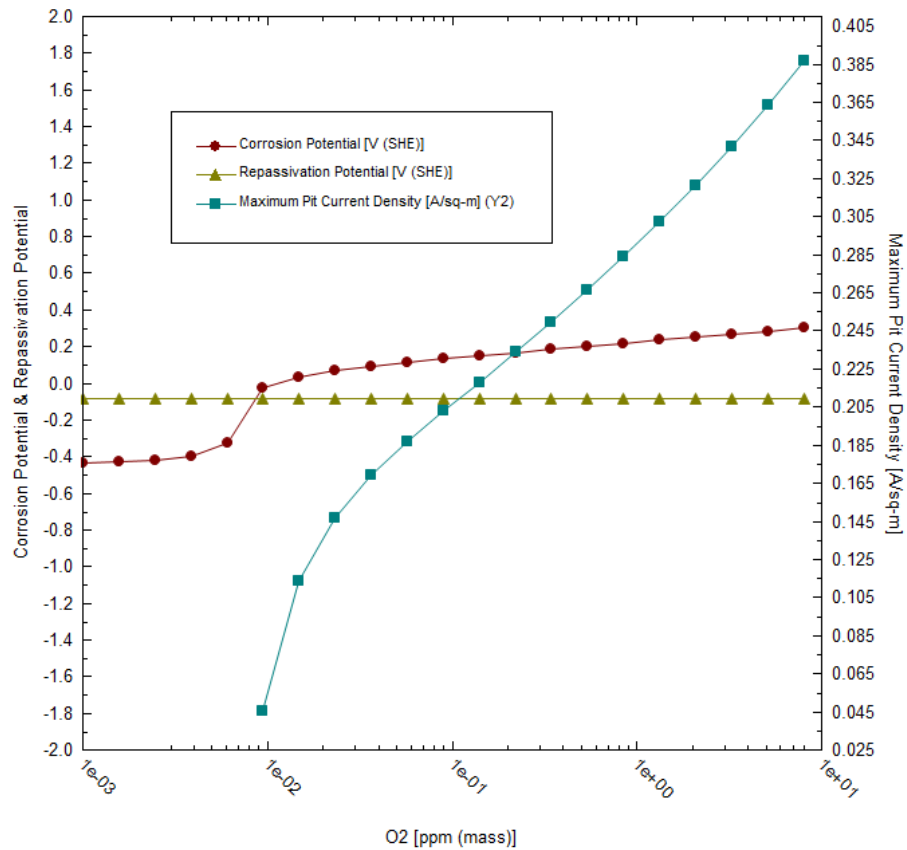
### Calculating Corrosion Rates for 2205

- ✓ Copy the **SS 316 vs O<sub>2</sub>** corrosion rate calculation and then paste it on the **Molecular Well H1** stream
- ✓ Change the name to **2205 vs O<sub>2</sub>**
- ✓ Change the contact surface to Duplex Stainless 2205
- ✓ **Calculate**
- ✓ Click on the **General Corr. Rate** tab (  **General Corr. Rate** ). This tab displays a plot showing the results of corrosion rate and pH as a function of O<sub>2</sub> concentration.
- ✓ Right click on the X-axis and change the scale to Logarithmic scale



The corrosion rate values are even smaller for alloy 2205. Is this alloy susceptible to localized corrosion?

- ✓ Click on the **Localized Corr.** tab (Localized Corr. ). This tab displays a plot showing the results of corrosion potential, repassivation potential and maximum pit current density values as a function of O2 concentration.
- ✓ Right click on the X-axis and change the scale to Logarithmic scale



This plot shows that at concentrations higher than ~1 ppm of O2 concentration the criterion  $E_{corr} > E_{rep}$  is met and localized corrosion is predicted to occur. Notice that the maximum pit current density values are lower in magnitude when compared to the pitting values of SS 316.

Based on the results obtained for the 3 different alloys under the same conditions the ranking of the alloys can be presented as follows: 2205 > SS 316 > Carbon Steel

## Stability Diagram of Carbon Steel when drilling with alkaline mud

Study the stability diagram of carbon steel when drilling with alkaline mud (pH 10-12) at 120 °C and 20 atm.

### Environment Creation

The chemical environment in which a particular metal will corrode needs to be entered before the stability analysis can be calculated, in this case the composition of the alkaline mud.

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-in alkaline mud	Stream Amount	Calculated
Framework	AQ	Temperature	120 °C
Calculation Type	Stability Diagram	Pressure	20 atm
Inflow units	Mass (g)	pH Range	0-14
		H2O	350 g
		Na2CO3	0.5 g
		NaOH	0.5 g
		Contact Surface	Fe

- ✓ Add a new **Stream**
- ✓ **Click** on the new Stream and press **<F2>** to change the name to *CS in alkaline mud*
- ✓ Change inflow units to mass

Inflows (mol)	
H2O	55.5082

Composition				Parameters		Corrosion	
	Variable	Basis		Units			
Inflow variables							
	Stream Amount	Moles		mol			
	Inflows	Mass		g			
Output variables							
	Aqueous Composition	Moles		mol			
	Vapor Composition	Concentration		mol			
	Solid Composition	Molar Concentration		mol			
	2nd Liquid Composition	Mass Fraction		mol			
	Total Composition	Mole Fraction		mol			

- ✓ Click **OK**
- ✓ Add the chemistry given in the table above
- ✓ Change the Temperature = 120 °C and Pressure = 20 bar
- ✓ 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**

**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.

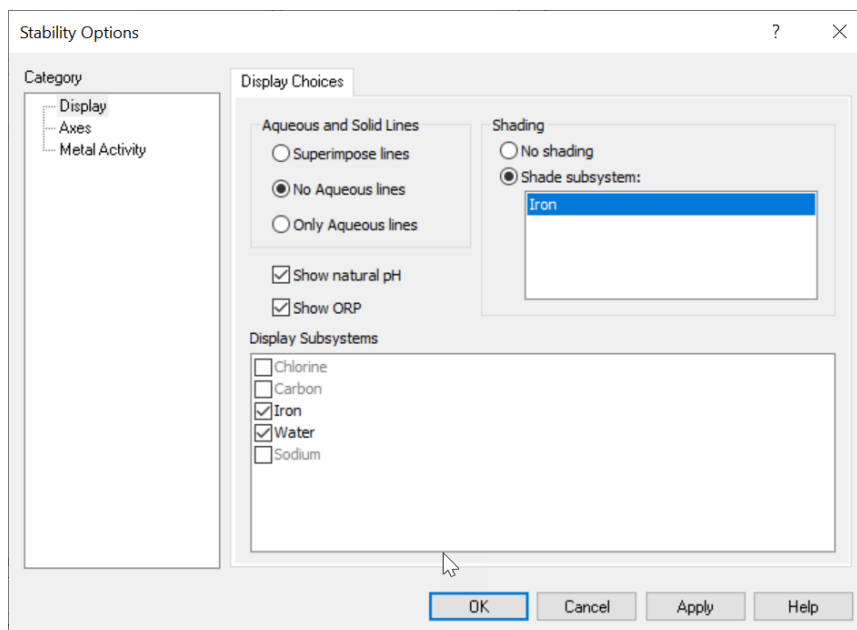
The only requirement before the calculate button can be clicked, is to select the '**Contact Surface**' that will be studied. The '**Contact Surface**' is the metallic material for which the stability is to be studied.

- ✓ Under the **Contact Surface** grid type **Fe**

Your screen should look like the image below:

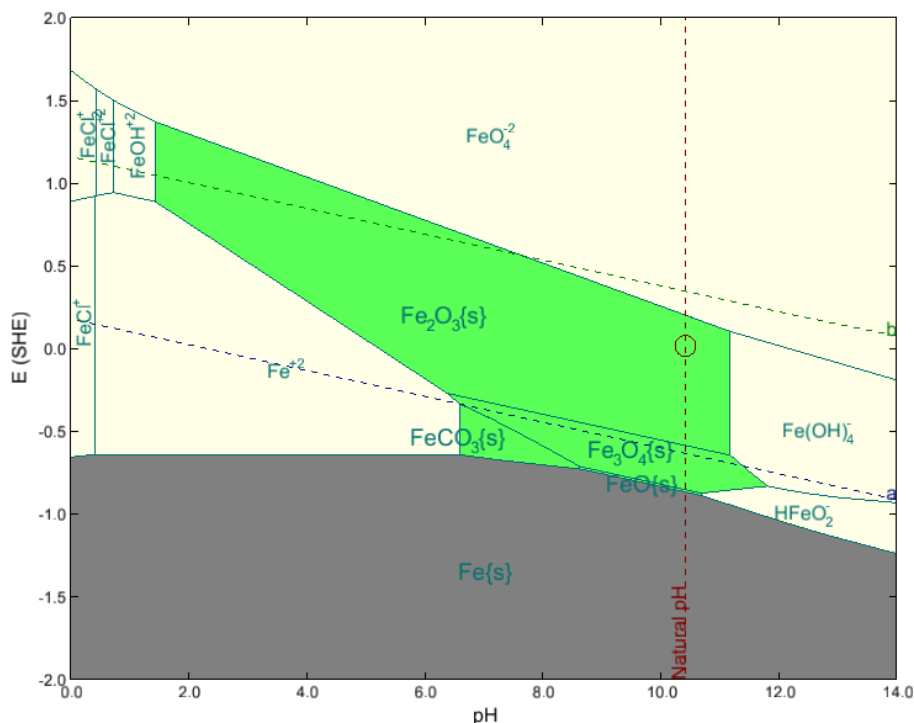
Variable	Value
Stream Parameters	
Stream Amount (mol)	19.4451
Temperature (°C)	120.000
Pressure (atm)	20.0000
Calculation Parameters	
Use Single Titrant	No
pH Acid Titrant	HCL
pH Base Titrant	NaOH
Inflows (g)	
H2O	350.000
Na2CO3	0.500000
NaOH	0.500000
Fe	0.0
Contact Surface (mol)	
Fe	

- ✓ Click on the **Specs...** button to modify the appearance of the diagram
- ✓ Select the option for **No Aqueous lines** and **Show ORP** and then Click OK



## Analyzing the Results

The Pourbaix Diagram for the Fe-Alkaline mud system at 120 °C and 20 atm should look like the image below:



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  $\text{Fe}^{2+}$ . If the pH is above 11, the boundary is at a lower potential for example, -1.0 V SHE at 12 pH.

The software computes that  $\text{Fe}_3\text{O}_4$  (magnetite) is stable between a pH range of ~6.4 and 12. This is also known as the *Passive Film* that protects the iron surface from active corrosion. At higher potentials, the software computes  $\text{Fe}_2\text{O}_3$  (hematite). Hematite is the dehydrated form of  $\text{Fe}(\text{OH})_3$  and  $\text{FeOOH}$ , two forms of rust. These phases provide less corrosion protection the iron surface than the magnetite. The software also computes that  $\text{FeCO}_3$  (siderite) is stable between a pH range of 6.5-8.6. These three 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  $\text{Fe}^{2+}$ . The software computes stability for this species from -0.6 V to 0.9 V SHE, at low pH, and it is no longer stable at pH 6.5. Active corrosion of the iron surface is predicted if the pH is between 0 and 6.5. 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 6.5 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 (10.42 pH, 0.015 V SHE) indicates that  $\text{Fe}_2\text{O}_3$  (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.  $\text{Fe}^{2+}$ .

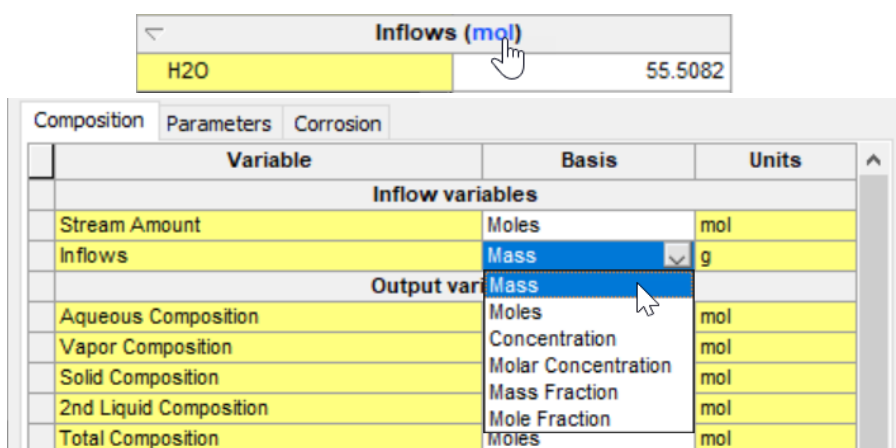
## Corrosion Rates under Acid Stimulation

In this example we are going to study the corrosion rate prediction/cumulative metal loss under acid stimulation (15% HCl) at 120°C and 400 atm (reservoir conditions). This prediction will calculate the corrosion rate when no inhibitor is added.

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.

Survey Calculation			
Calculation Settings		Stream Composition and Conditions	
Stream Name	Stimulation Fluid	Stream Amount	Calculated
Framework	AQ	Temperature	120 °C
Calculation Type	Survey	Pressure	400 atm
Inflow units	Mass (g)	H2O	850 g
		HCl	150 g
		Fe	0 g

- ✓ Add a new **Stream**
- ✓ **Click** on the new Stream and press **<F2>** to change the name to *Stimulation Fluid*
- ✓ Change inflow units to mass




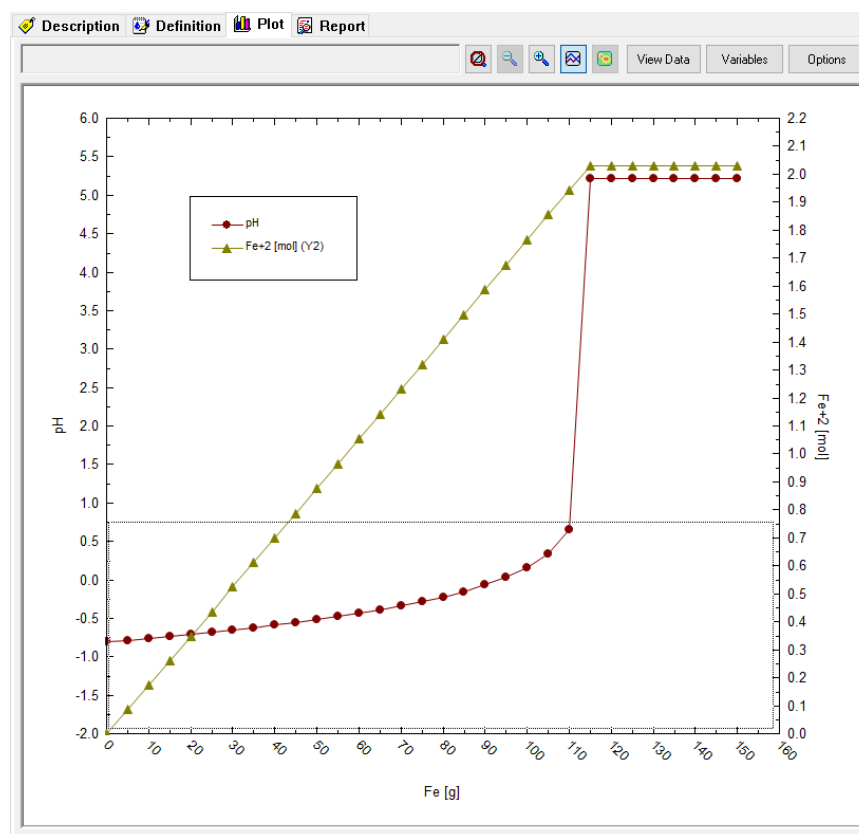
- ✓ Click **OK**
- ✓ Add the chemistry given in the table above
- ✓ Change the Temperature = 120 °C and Pressure = 400 bar



- ✓ Turn ON **RedOx** reactions
- ✓ Click on the **Add Calculation** button and add a **survey calculation**
- ✓ **Click** on the new icon *Survey* and press **<F2>** to change the name to **Fe Survey**
- ✓ Select Survey by **Composition**
- ✓ Click on the Specs button and add the following Survey Range: **Fe** - 0 to 150 g every 5 g (increment)

## Analyzing the Results

- ✓ Click on the  **Plot** tab. The default plot is the pH as a function of consumed iron in g.



This plot is the cumulative dissolution of iron when in contact with an acidic stimulation fluid. Above 110 g of Fe, the dissolution of Fe reaches a plateau, and the pH remains constant. This indicates a saturation of  $\text{Fe}^{+2}$  ions (you can confirm this by adding  $\text{Fe}^{+2}$  ions in the Y2 axis) and indicates the formation of a passive film on the metallic surface.

Notice that the dissolution of Fe happens at the pH range of -0.8 to 0.65. We can find out the corrosion rate values by running a pH survey.

- ✓ Click on the **Stimulation Fluid** stream and add a **Corrosion Rate** calculation
- ✓ **Click** on the new icon *Rates* and change the name to **Fe CR**
- ✓ Select Survey by **pH**
- ✓ Click on the **Specs** button and add the following Survey Range: **pH** : -0.8 to 0.65 every 0.05 (increment)
- ✓ Select **Carbon Steel G10100 (generic)** as the **contact surface**
- ✓ Click **OK** and **Calculate**

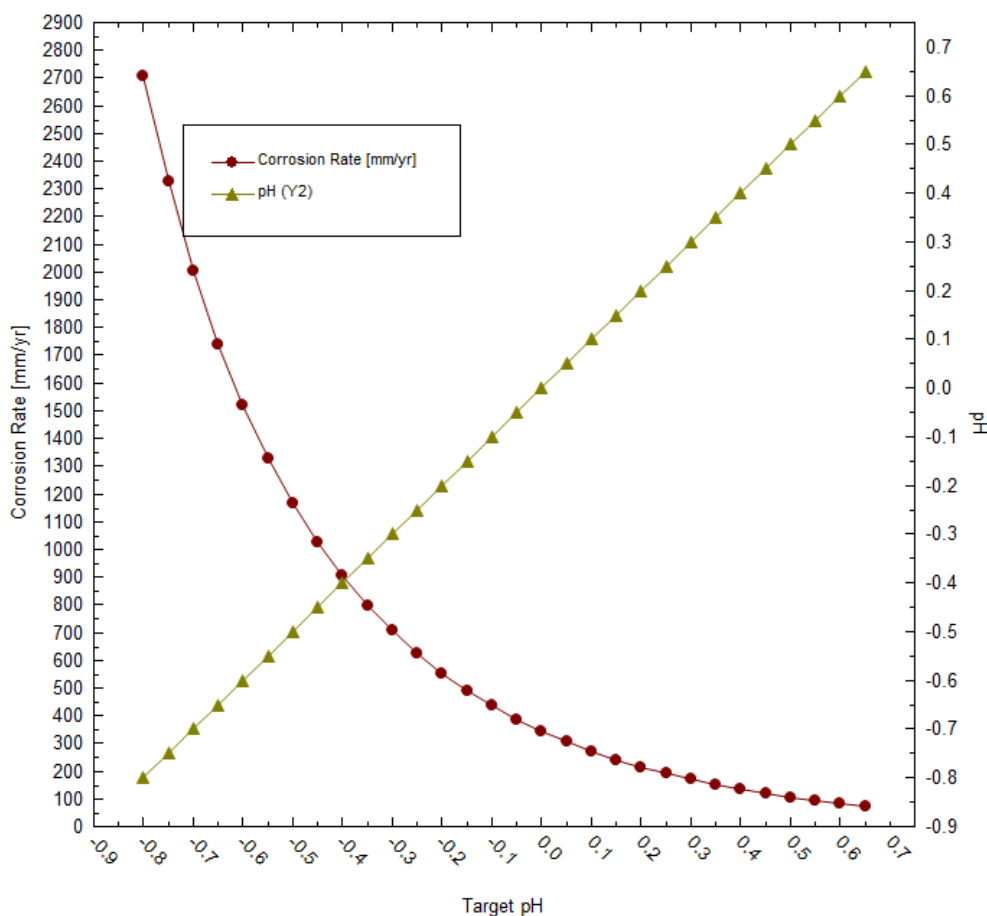
## Analyzing the Results

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



The default plot shows the corrosion rate (red curve) as a function of the target pH.

The corrosion rate values at the lowest pH are in the 1000ths order of magnitude in mm/year. As the highest pH value of 0.65, the corrosion rate decreased one order of magnitude, i.e., approx. 75 mm/year. These results show the importance of adding a corrosion inhibitor when performing acid stimulation.



## Autoclaves for Corrosion Testing

Autoclave corrosion testing is used to recreate the downhole conditions so that the corrosivity of production fluids or the performance of corrosion inhibitors can be tested. Proper materials testing needs to be performed before they are approved for service.

When experiments are performed at high pressures and salinities, species reactivity deviates from ideality. That is, a gas component (e.g.,  $\text{H}_2\text{S}$  vap) or a species in solution (e.g.,  $\text{H}_2\text{S}$  aq), will behave differently at high pressures or in saline solution, than at low pressure or dilute solution, even if their partial pressure or concentration is the same in both situations.

Thus, as it relates to corrosion experiments, accounting for the change in behavior (termed fugacity in the vapor and activity in the brine) of aggressive species is critical to recreating downhole environments. This makes

accurate autoclave charging a challenging task, since relying on ideal or simplified models can introduce errors and cause the experiment to deviate from actual conditions.

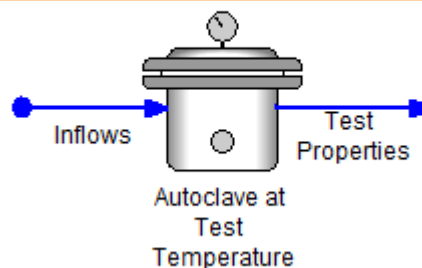
In this example we are going to recreate two different autoclave experiments: One scenario will represent low pressure conditions and a second scenario will represent high pressure conditions; and then evaluate the effect of fugacity on corrosion rates of carbon steel.

## First Case Scenario: Low Pressure

### Autoclave Conditions and Specifications

- Testing Solution: Test NACE TM0177 Modified **Solution B**
- Solution pH=3.5
- Autoclave volume: 5 L
- Final conditions:  $T_f = 25^\circ\text{C}$  and  $P_f = 5,000 \text{ mbar}$
- Partial Pressures of key gases at final conditions:
  - $\text{PCO}_2 = 500 \text{ mbar}$
  - $\text{PH}_2\text{S} = 500 \text{ mbar}$

6.2.2 Test Solution B shall consist of 5.0 wt% sodium chloride, 2.5 wt% glacial acetic acid, and 0.41 wt% sodium acetate dissolved in distilled or deionized water



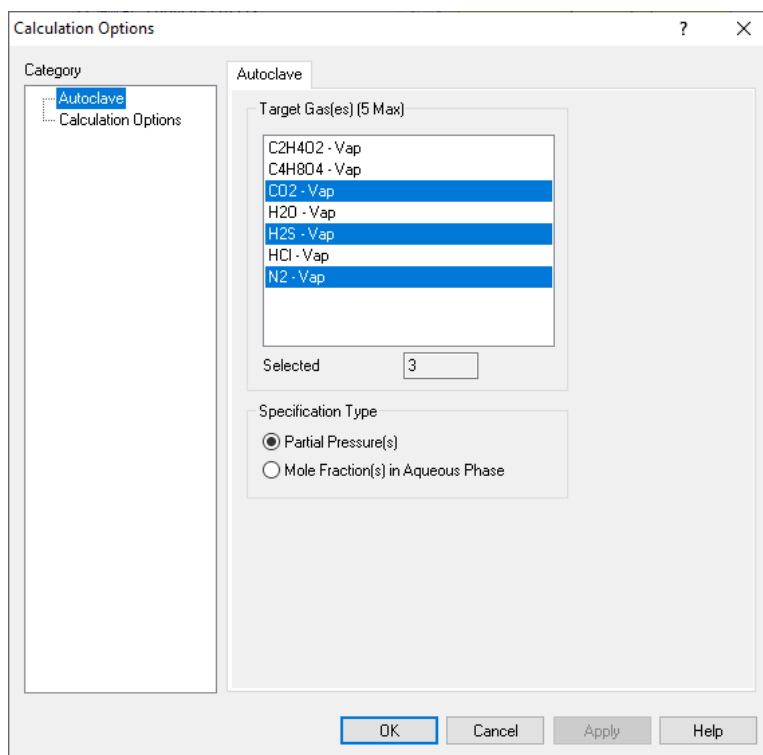
Use the inputs and parameters from the table below to create the stream's composition. Certain inputs, such as the name style, units, etc. will require further adjustments, and will be described as necessary.

Solution B			
Calculation Settings		Stream Composition and Conditions	
Stream Name	Solution B	Stream Amount	1 kg
Name Style	Display Formula	Temperature	$25^\circ\text{C}$
Unit Set	Metric, Batch, Mass Fraction Change <b>pressure</b> and <b>partial pressures</b> and <b>fugacities</b> to mbar	Pressure	1013.25 mbar
Framework	MSE-SRK	H <sub>2</sub> O	92.09 mass%
Calculation Type	Autoclave	NaCl	5 mass%
		C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>	2.5 mass%
		Na[C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ]	0.41 mass%
		CO <sub>2</sub>	0 mass%
		H <sub>2</sub> S	0 mass%
		N <sub>2</sub>	0 mass%

### Building the Case

- ✓ Add a stream and rename it **Solution B**
- ✓ Change the units to **metric | batch | mass fraction** and **pressure** and **partial pressures** and **fugacities** to mbar
- ✓ Select the **MSE-SRK** thermodynamic framework

- ✓ Deselect the **L2** phase (*there is not an organic phase in this stream*)
- ✓ Add inflows to reconstruct **solution B**, CO<sub>2</sub>, H<sub>2</sub>S and N<sub>2</sub> (see table above)
- ✓ Add a **single point** calculation and select **Autoclave**
- ✓ Go to **specs...** select partial pressures for CO<sub>2</sub>-Vap, H<sub>2</sub>S-Vap and N<sub>2</sub>-Vap



- ✓ Click OK
- ✓ In the **Definition** tab, enter the partial pressures for CO<sub>2</sub> and H<sub>2</sub>S, vessel volume, and final conditions (T and P) as shown below

Variable	Value
Stream Parameters	
Stream Amount (g)	1000.00
Ambient: Temperature (°C)	25.0000
Ambient: Pressure (mbar)	
Calculation Parameters	
Final Temperature (°C)	25.0000
Final Pressure (mbar)	5000.00
Vessel Volume (L)	5.00000
Partial Pressure: CO2 (mbar)	500.000
Partial Pressure: H2S (mbar)	500.000
Partial Pressure: N2 (mbar)	
Compute results at which condition	Final
Inflows (g)	
H2O	920.900
NaCl	50.0000
C2H4O2	25.0000
Na[C2H3O2]	4.10000
CO2	0.0
H2S	0.0
N2	0.0

- ✓ Select the option *Compute results at **final** conditions*
- ✓ Click on the **Calculate** button

## Analyzing the Results

After the calculation is done check the **Summary** box. In the **Summary** section you can see two pieces of information: 1. That at the final conditions (25 C and 5,000 mbar) there are two phases, a liquid phase, and a vapor phase. 2. The pH of the liquid phase is 3.47. This means that the buffer is doing a good job of keeping the pH constant at around the 3.5 pH value. The summary box, however, doesn't give information of the composition of the gas mix (CO<sub>2</sub>, H<sub>2</sub>S, and N<sub>2</sub>) needed to reach the final conditions nor information about partial pressure, fugacities, and fugacity coefficients of the vapor species.

- ✓ Click on the **Report** tab.

The first piece of information is to find out the composition of the gas-mix needed to reach the final conditions.

- ✓ Go to **Stream Inflows** table

This table shows the amount in grams of each one of the gas components needed to load the autoclave at ambient conditions, so that we can reach the desired final partial pressures of CO<sub>2</sub> and H<sub>2</sub>S.

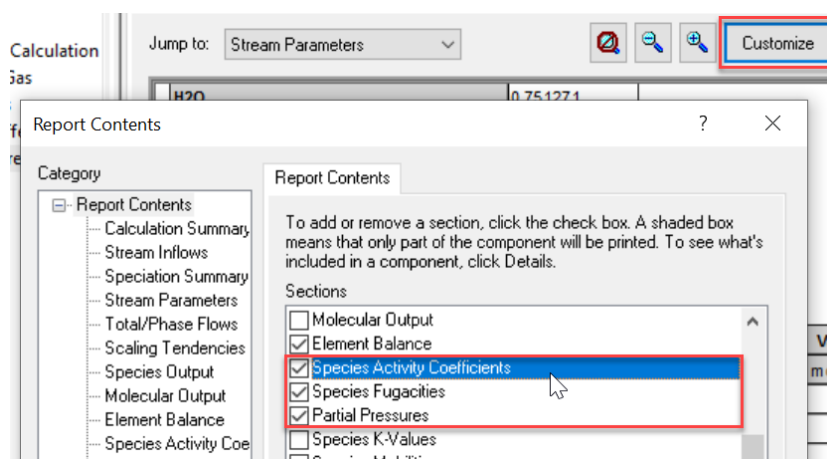
### Stream Inflows

Row Filter Applied: Only Non Zero Values

	Input	Output
Species	g	g
H2O	920.900	920.900
NaCl	50.0000	50.0000
C2H4O2	25.0000	25.0000
Na[C2H3O2]	4.10000	4.10000
CO2	0.0	4.16402
H2S	0.0	4.14090
N2	0.0	18.2241

The next step is to study the partial pressures and fugacities of the gases in the system at the final conditions. To do this we need to enable the partial pressures and fugacity tables in the report.

- ✓ Click on the **customize** button and enable (check) the following tables: 1. Species activity coefficients, 2. Species Fugacities and 3. Partial pressures



- ✓ Click OK to accept the changes
- ✓ Go to the **Partial Pressure** table. The partial pressure for CO2 and H2S is 500 mbar, as specified for the final conditions.

### Partial Pressures

Row Filter Applied: Only Non Zero Values

Species	mbar
C4H8O4	1.87147e-4
C2H4O2	0.289932
CO2	500.008
H2O	31.0924
H2S	500.0
HCl	1.07846e-7
N2	3968.61

What is the effective pressure, or fugacity of CO2 and H2S at the final pressure? We can check the **fugacity** table.

- ✓ Go to the **Species Fugacities** table. Notice that the fugacities are approx. 10 mbar lower than the partial pressure

#### Species Fugacities

Row Filter Applied: Only Non Zero Values

Species	mbar
C4H8O4	1.73245e-4
C2H4O2	0.268691
CO2	490.397
H2O	30.4604
H2S	489.71
HCl	1.05647e-7
N2	3970.54

The fugacity coefficient of CO2 and H2S at this low-pressure system is ~0.98, closer to an ideal gas behavior ( $\phi=1$ ).

#### Species Activity/Fugacity Coefficients

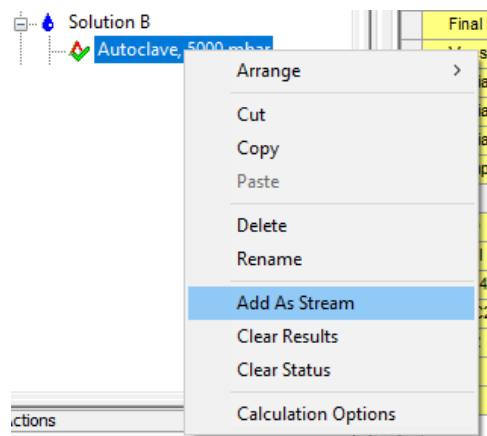
Row Filter Applied: Only Non Zero Values

	$\gamma$	$\gamma$	Fugacity Coefficients
Species	x-based	m-based	
C4H8O4 - Liq1	0.973926	0.93274	
C4H8O4 - Vap			0.925718
C2H4O2 - Vap			0.926737
CO2 - Vap			0.980779
H2O - Vap			0.979673
H2S - Vap			0.979421
HCl - Vap			0.979609
N2 - Vap			1.00049

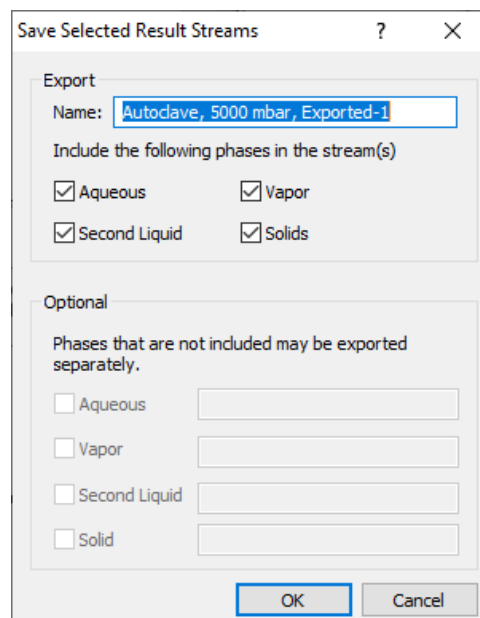
## Corrosion Rate Calculations

Let's calculate the corrosivity of the liquid phase on carbon steel.

- ✓ Right click on the **Autoclave, 5000 mbar** single point calculation and **select** the option **Add as Stream**




- ✓ This opens a new window. **Select** the phases of interest that you want to export, in this case we are going to select all the phases, since we want to export all the contents present in the autoclave at final conditions.
- ✓ Leave the default name and then click **OK**



- ✓ Change the Thermodynamic Framework to **AQ**
- ✓ Add a **Single Point Corrosion Rate** Calculation
- ✓ Rename the new corrosion rate calculation as **CR-CS1018 - 5000 mbar**
- ✓ **Calculate**

## 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	25.0000	0.992290	3.49916

The predicted corrosion rate of carbon steel at 25 °C and 5,000 mbar is ~1 mm/year.

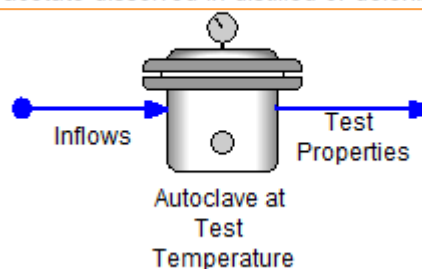
Let's study the high-pressure scenario.

## Second Case Scenario: High Pressure

### Autoclave Conditions and Specifications

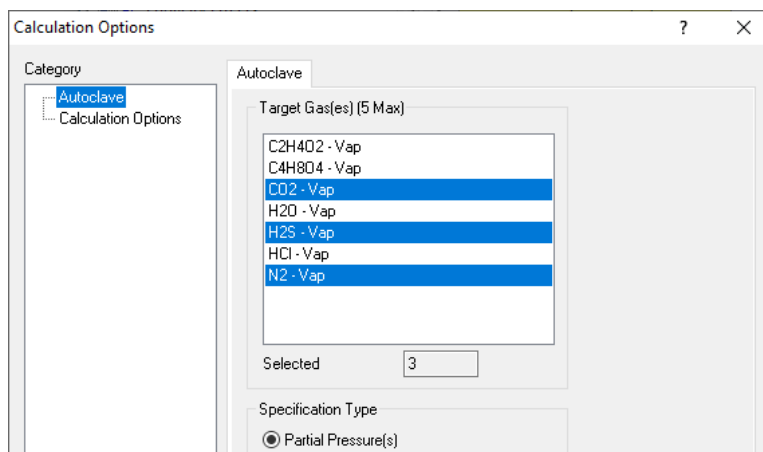
- Testing Solution: Test NACE TM0177 Modified **Solution B**
- Solution pH=3.5
- Autoclave volume: 5 L
- Final conditions:  $T_f = 25^\circ\text{C}$  and  $P_f = 50,000$  mbar
- Partial Pressures of key gases at final conditions:
  - $\text{PCO}_2 = 15,000$  mbar
  - $\text{PH}_2\text{S} = 15,000$  mbar

6.2.2 Test Solution B shall consist of 5.0 wt% sodium chloride, 2.5 wt% glacial acetic acid, and 0.41 wt% sodium acetate dissolved in distilled or deionized water



### Building the case

- ✓ Select **Solution B**, add a **single point** calculation and select **Autoclave**
- ✓ Go to **specs...** select partial pressures for CO<sub>2</sub>-Vap, H<sub>2</sub>S-Vap and N<sub>2</sub>-Vap



- ✓ Click **OK**
- ✓ In the **Definition** tab, enter the partial pressures for CO<sub>2</sub> and H<sub>2</sub>S, vessel volume, and final conditions (T and P) as shown below



Variable	Value
Stream Parameters	
Stream Amount (kg)	1.00000
Ambient: Temperature (°C)	25.0000
Ambient: Pressure (mbar)	
Calculation Parameters	
Final Temperature (°C)	25.0000
Final Pressure (mbar)	50000.0
Vessel Volume (L)	5.00000
Partial Pressure: CO2 (mbar)	15000.0
Partial Pressure: H2S (mbar)	15000.0
Partial Pressure: N2 (mbar)	
Compute results at which condition	Final

- ✓ Select the option *Compute results at **final** conditions*
- ✓ Click on the **Calculate** button

## Analyzing the Results

- ✓ Check the pH in the **summary** box. At these new conditions the pH remains constant at a pH-3.5.
- ✓ Click on the **Report** tab and go to **Stream Inflows** table to check the composition of the gas-mix at these high-pressure conditions.

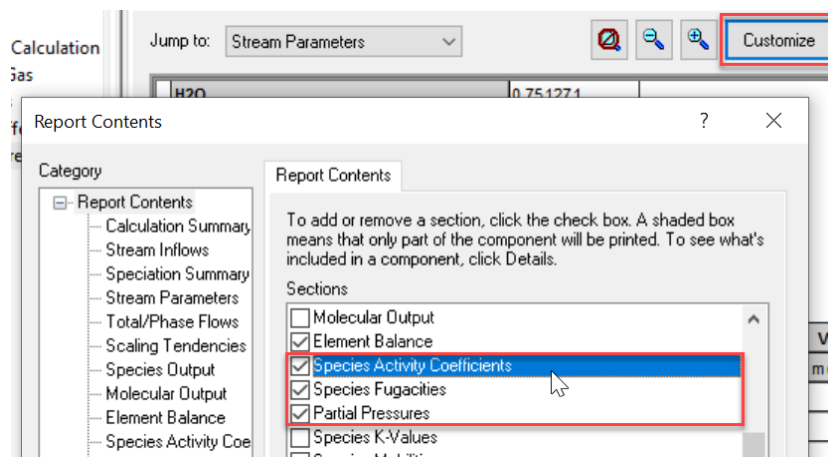
### Stream Inflows

Row Filter Applied: Only Non Zero Values

	Input	Output
Species	mass %	mass %
H2O	92.0900	66.9885
NaCl	5.00000	3.63712
C2H4O2	2.50000	1.81856
Na[C2H3O2]	0.410000	0.298244
CO2	0.0	10.1449
H2S	0.0	9.33605
N2	0.0	7.77670

The next step is to study the partial pressures and fugacities of the gases in the system at the final conditions. To do this we need to enable the partial pressures and fugacity tables in the report.

- ✓ **Click** on the **customize** button and enable (check) the following tables: 1. Species activity coefficients, 2. Species Fugacities and 3. Partial pressures



- ✓ Click OK to accept the changes
- ✓ Go to the **Partial Pressure** table. The partial pressure for CO<sub>2</sub> and H<sub>2</sub>S is 15,000 mbar, as specified for the final conditions.

### Partial Pressures

Row Filter Applied: Only Non Zero Values

Species	mbar
C <sub>4</sub> H <sub>8</sub> O <sub>4</sub>	5.30775e-4
C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>	0.849002
CO <sub>2</sub>	14999.8
H <sub>2</sub> O	46.499
H <sub>2</sub> S	15000.0
HCl	1.31106e-7
N <sub>2</sub>	19952.8

- ✓ Go to the **Species Fugacities** table. Notice that the fugacity of CO<sub>2</sub> is 3250 mbar lower and the fugacity of H<sub>2</sub>S is 4094.5 mbar lower than the specified partial pressures.

### Species Fugacities

Row Filter Applied: Only Non Zero Values

Species	mbar
C <sub>4</sub> H <sub>8</sub> O <sub>4</sub>	1.53309e-4
C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>	0.254536
CO <sub>2</sub>	11750.3
H <sub>2</sub> O	30.7074
H <sub>2</sub> S	10905.5
HCl	9.87174e-8
N <sub>2</sub>	21372.4

The fugacity coefficient of CO<sub>2</sub> and H<sub>2</sub>S at this high-pressure system are ~0.78 and ~0.72, respectively, no longer behaving as ideal gases.

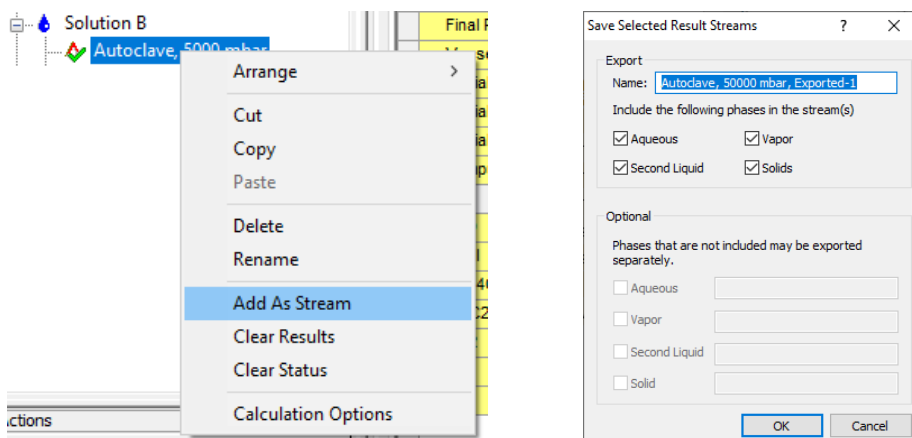
## Species Activity/Fugacity Coefficients

Row Filter Applied: Only Non Zero Values

	$\gamma$	$\gamma$	Fugacity Coefficients
Species	x-based	m-based	
C4H8O4 - Liq1	0.945317	0.885965	
C4H8O4 - Vap			0.28884
C2H4O2 - Vap			0.299806
CO2 - Vap			0.783364
H2O - Vap			0.660388
H2S - Vap			0.727035
HCl - Vap			0.752961
N2 - Vap			1.07115


## Corrosion Rate Calculations

- ✓ Right click on the **Autoclave, 50000 mbar** single point calculation and **select** the option **Add as Stream**



- ✓ This opens a new window. **Select** the phases of interest that you want to export, in this case we are going to select all the phases, since we want to export all the contents present in the autoclave at final conditions.
- ✓ Leave the default name and then click **OK**
- ✓ Change the Thermodynamic Framework to **AQ**
- ✓ Add a **Single Point Corrosion Rate** Calculation
- ✓ Rename the new corrosion rate calculation as **CR-CS1018 - 50000 mbar**
- ✓ **Calculate**

## 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	25.0000	2.08441	3.48017

The predicted corrosion rate of carbon steel at 25 °C and 50,000 mbar is ~2 mm/year.

The results of the two simulations (low pressure and high pressure) are summarized in the table below.

Low Pressure		High Pressure	
T	25 C	T	25 C
P	5,000 mbar	P	50,000 mbar
P <sub>CO2</sub>	500 mbar	P <sub>CO2</sub>	15,000 mbar
P <sub>H2S</sub>	500 mbar	P <sub>H2S</sub>	15,000 mbar
x <sub>H2S</sub>	0.135 mass%	x <sub>H2S</sub>	2.95 mass%
x <sub>CO2</sub>	0.056 mass %	x <sub>CO2</sub>	1.29 mass%
pH	3.5	pH	3.5
CR	0.98 mm/y	CR	2.06 mm/y

Notice that in these two examples the pH of the solution remained constant, yet the corrosion rate results were different. At high pressure the corrosion rate was two times the corrosion rate value at low pressure. In this case the corrosion rate values are not pH dependent.

You can further investigate what is causing the differences by studying the half-reactions that are dominant at the metallic/solution interface by using the polarization curves.

## Effect of Fugacity on Corrosion Rates

Fugacity was introduced by G. N. Lewis in 1901 and became widely used after the very influential textbook Thermodynamics, by Lewis and Randall in 1923.

Lewis describes ...fugacity in an analogy with temperature. Equilibrium requires that heat must flow such that temperature is the same in all parts of the system. Matter must flow such that chemical potentials are the same in all parts of the system. A dissolved gas escaping to achieve vapor pressure equilibrium is an “escaping tendency” or fugacity.

We are going to create an example to explain the impact of fugacity on solution chemistry and on corrosion rates.

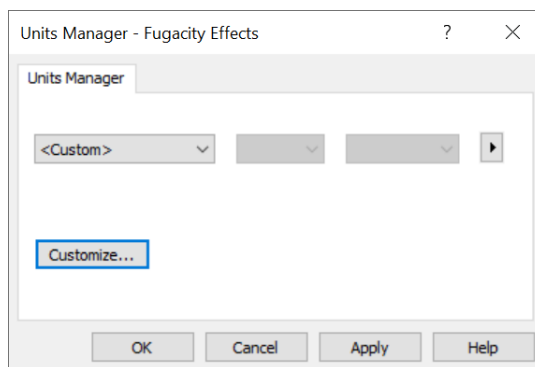
## Fugacity Effects – High Pressure

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.

Fugacity Effects – High Pressure			
Calculation Settings		Stream Composition and Conditions	
Stream Name	Fugacity Effects	Stream Amount	Calculated
Name Style	Display Formula	Temperature	25°C
Unit Set	Metric, Batch, Moles Change all the <b>output variables</b> to <b>mole%</b>	Pressure	400 atm
Framework	AQ	H2O	55.5082 moles
Calculation Type	Isothermal Calculation	CO2	5 mole
		N2	500 moles
		NaCl	1 mole

First, we are going to build a high pressure (400 atm) scenario.

- ✓ Add a new **Stream**
- ✓ **Click** on the new Stream and press **<F2>** to change the name to ***Fugacity Effects***
- ✓ Select the **MSE-SRK** thermodynamic Framework
- ✓ **Click** on the **Names Manager** Icon and select the **Formula** option
- ✓ **Click** on the **Units Manager** Icon, and select Metric, Batch, Mole
- ✓ **Click** on the **customize** button in the units manager



- ✓ **Change** the output variables to Mole Fraction as shown in the image below

Edit Units - Fugacity Effects

☒ Batch System ☐ Flowing System

Composition Parameters Corrosion

Variable	Basis	Units
<b>Inflow variables</b>		
Stream Amount	Moles	mol
Inflows	Moles	mol
<b>Output variables</b>		
Aqueous Composition	Mole Fraction	mole %
Vapor Composition	Mole Fraction	mole %
Solid Composition	Moles	mol
2nd Liquid Composition	Moles	mol
Total Composition	Moles	mol
<b>Basis options</b>		
Moles		mol
Mass		g
Volume		L
Concentration		mg/L
Molar Concentration		mol/L
Mass Fraction		mass %
Mole Fraction		mole %

OK Cancel Help

- ✓ Click **OK** to accept the changes
- ✓ Enter the composition, temperature and pressure of the stream given in the table above
- ✓ Go to the **Add Calculation** button and select **Single Point** calculation and rename it **High Pressure**

Description Definition Report

Variable	Value
<b>Stream Parameters</b>	
Stream Amount (mol)	561.508
Temperature (°C)	25.0000
Pressure (atm)	400.000
<b>Inflows (mol)</b>	
H2O	55.5082
CO2	5.00000
N2	500.000
NaCl	1.00000

Type of calculation: Isothermal

Calculate

Summary

Unit Set: <Custom>

Automatic Chemistry Model

MSE-SRK (H3O+ ion) Databanks:

MSE-SRK (H3O+ ion)

MSF (H3O+ ion)

- ✓ Click on the **Calculate** button

## Analyzing the Results

After the calculation is done check the **Summary** box. In the **Summary** section you can see two pieces of information: 1. That at these conditions there are two phases, a liquid phase, and a vapor phase. 2. The pH of the liquid phase, which is 3.67. The summary box, however, doesn't give information about partial pressure, fugacities, and fugacity coefficients of the vapor species.

Software interface showing the **Report** tab. The left panel displays input parameters:

Variable	Value
<b>Stream Parameters</b>	
Stream Amount (mol)	561.508
Temperature (°C)	25.0000
Pressure (atm)	400.000
<b>Inflows (mol)</b>	
H2O	55.5082
CO2	5.00000
N2	500.000
NaCl	1.00000

The right panel shows the **Summary** section:

Type of calculation: Isothermal

Calculate [icon]

Unit Set: <Custom>

Automatic Chemistry Model  
 MSE-SRK (H3O+ ion) Databanks:  
 MSE-SRK (H3O+ ion)  
 MSE (H3O+ ion)  
 Second Liquid phase  
 Using Helgeson Direct

Isothermal Calculation  
 25.0000 °C 400.000 atm

**Phase Amounts**

Aqueous	57.5832 mol
Vapor	504.925 mol
Solid	0.0 mol
2nd Liquid	0.0 mol

**Aqueous Phase Properties**

pH	3.66958
Ionic Strength	0.0173698 mol/mol
Density	1.05230 g/ml

- ✓ Click on the **Report** tab. The first piece of information to study is the composition of the vapor phase.
- ✓ Go to the **Species Out (True Species)** table

#### Species Output (True Species)

Row Filter Applied: Only Non Zero Values

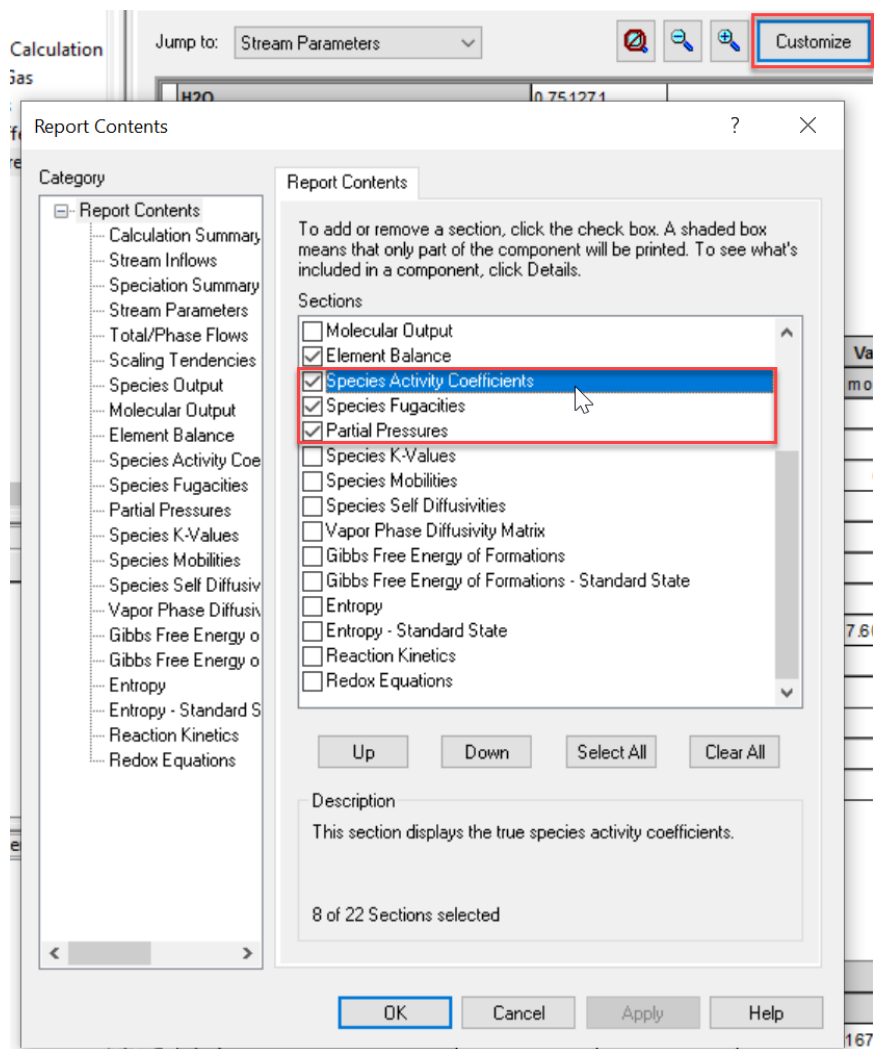
Column Filter Applied: Only Non Zero Values

	Total	Liquid-1	Vapor
	mol	mole %	mole %
N2	500.0	0.210178	99.0007
H2O	55.5078	96.2592	0.0155857
CO2	4.99979	0.0566456	0.983745
Na+1	1.0	1.73662	
Cl-1	1.0	1.73662	
H3O+1	2.08686e-4	3.62408e-4	
HCO3-1	2.08686e-4	3.62407e-4	
CO3-2	4.06477e-10	7.05895e-10	
HCl	2.41289e-10	3.95159e-12	4.73366e-11
OH-1	1.08719e-10	1.88804e-10	
NaOH	1.71114e-17	2.97159e-17	
NaOHCO3-2	1.01225e-21	1.75788e-21	
Total (by phase)	562.508	100.0	100.0

Notice that at these conditions most of the CO<sub>2</sub> is in the vapor phase. Notice that at these conditions some of the H<sub>2</sub>O also goes to the vapor phase. Additionally, the composition of the aqueous phase shows the composition of dissolved molecular CO<sub>2</sub> and HCO<sub>3</sub><sup>-1</sup> species in solution. This liquid composition will be used to perform corrosion rate calculations.

The next step is to study the partial pressures and fugacities of the gases in the system. To do this we need to enable the partial pressures and fugacity tables in the report.

- ✓ **Click** on the **customize** button and enable (check) the following tables: 1. Species activity coefficients, 2. Species Fugacities and 3. Partial pressures



- ✓ **Click** OK to accept the changes
- ✓ **Go** to the **Partial Pressure** table. The partial pressure of CO<sub>2</sub> at this high-pressure condition is 3.93 atm.

### Partial Pressures

Row Filter Applied: Only Non Zero Values

Species	atm
CO <sub>2</sub>	3.93498
H <sub>2</sub> O	0.0623427
HCl	1.89346e-10
N <sub>2</sub>	396.003

What is the effective pressure, or fugacity of CO<sub>2</sub> at this high pressure? We can check the **fugacity** table.



- ✓ Go to the **Species Fugacities** table. Notice that the calculated effective pressure is almost half the partial pressure value, i.e., 1.97 atm.

### Species Fugacities

Row Filter Applied: Only Non Zero Values

Species	atm
CO2	1.97845
H2O	0.0403507
HCl	9.4171e-11
N2	459.466

We can confirm that the calculated fugacity coefficient for the CO2 in the vapor phase is 0.5.

### Species Activity/Fugacity Coefficients


Row Filter Applied: Only Non Zero Values

	$\gamma$	$\gamma$	Fugacity Coefficients
Species	x-based	m-based	
Cl-1	0.68536	0.659722	
CO2 - Liq1	1.25884	1.21175	
CO2 - Vap			0.502785
H2O - Vap			0.647241
HCl - Vap			0.497348
N2 - Vap			1.16026

Now that we have studied both the speciation in the liquid phase and the composition of the vapor phase, we can go ahead and calculate the corrosivity of this environment on carbon steel.

- ✓ Click on the **Fugacity Effects** stream and **add a corrosion rate** calculation, and select **single point rate**
- ✓ Rename this new corrosion rate calculation as **CR High P**
- ✓ **Change** the thermodynamic framework to AQ
- ✓ Leave the default contact surface as **Carbon Steel G10100 (generic)**
- ✓ Click on the **calculate** button

## 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.

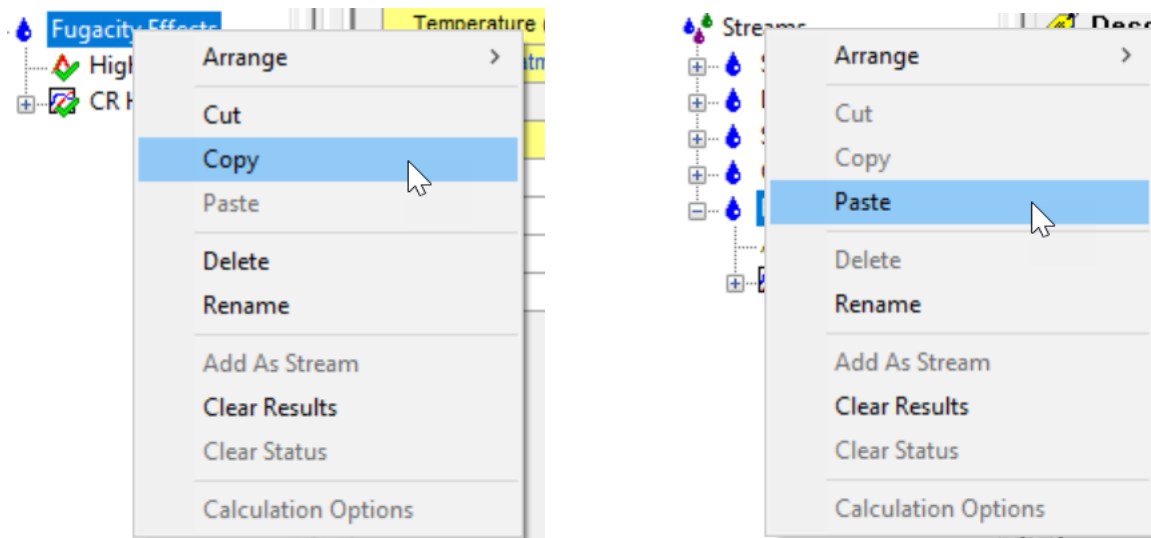
	Temperature	Corrosion Rate	pH
	°C	mm/yr	
1	25.0000	1.44118	3.60806

The predicted corrosion rate of carbon steel at 25 °C and 400 atm is ~1.44 mm/year.

## Fugacity Effects – Low Pressure

The next step is to calculate the corrosion rate of carbon steel simulating the same partial pressure of CO<sub>2</sub> but at a lower total pressure.

- ✓ **Copy** and then **paste** the *Fugacity Effects* stream



- ✓ **Rename** the pasted stream as **Partial Pressures**
- ✓ **Change** the name of the single point calculation from **High Pressure** to **Low Pressure**
- ✓ **Change** the total pressure of the stream to 4 atm
- ✓ **Zero out** the composition of N<sub>2</sub> gas (the final definition should look like the image below)

Variable	Value
Stream Parameters	
Stream Amount (mol)	61.5082
Temperature (°C)	25.0000
Pressure (atm)	4.00000
Inflows (mol)	
H <sub>2</sub> O	55.5082
CO <sub>2</sub>	5.00000
N <sub>2</sub>	0.0
NaCl	1.00000

- ✓ Click on the **Calculate** button

After the calculation is done check the **Summary** box. At these conditions there are two phases, a liquid phase, and a vapor phase. The pH of the liquid phase is 3.50.

- ✓ Click on the **Report** tab.

Let's check the partial pressures and fugacities of the gases in the system.

- ✓ **Go to the Partial Pressure table.** The partial pressure of CO<sub>2</sub> at this high-pressure condition is 3.97 atm.

#### Partial Pressures

Row Filter Applied: Only Non Zero Values

Species	atm
CO <sub>2</sub>	3.96861
H <sub>2</sub> O	0.0313857
HCl	1.02896e-10

- ✓ **Go to the Species Fugacities table.** Notice that the calculated effective pressure is very close in value to the partial pressure, i.e. 3.89 atm.

#### Species Fugacities

Row Filter Applied: Only Non Zero Values

Species	atm
CO <sub>2</sub>	3.88956
H <sub>2</sub> O	0.0302361
HCl	1.00676e-10

The fugacity coefficient of CO<sub>2</sub> at this low pressure system is 0.98, closer to an ideal gas behavior ( $\phi=1$ ).

#### Species Activity/Fugacity Coefficients

Row Filter Applied: Only Non Zero Values

	$\gamma$	$\gamma$	Fugacity Coefficients
Species	x-based	m-based	
Cl-1	0.667004	0.642572	
CO <sub>2</sub> - Liq1	1.25949	1.21335	
CO <sub>2</sub> - Vap			0.980079
H <sub>2</sub> O - Vap			0.963373
HCl - Vap			0.978422

Let's calculate the corrosivity of the liquid phase on carbon steel.

- ✓ Click on the **Partial Pressure** stream and **add a corrosion rate** calculation, and select **single point rate**
- ✓ Rename this new corrosion rate calculation as **CR Low P**
- ✓ Make sure the thermodynamic framework is AQ
- ✓ Leave the default contact surface as **Carbon Stell G10100 (generic)**
- ✓ Click on the **calculate** button

### 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	25.0000	3.97815	3.44404

The predicted corrosion rate of carbon steel at 25 °C and 4 atm is ~3.98 mm/year.

The results of the two simulations (low pressure and high pressure) are summarized in the table below.

Low Pressure		High Pressure	
T	25 C	T	25 C
P	4.00 atm	P	400 atm
$P_{CO_2}$	3.97 atm	$P_{CO_2}$	3.93 atm
$f_{CO_2}$	3.88 atm	$f_{CO_2}$	2.099 atm
$\phi_{CO_2}$	0.98	$\phi_{CO_2}$	0.53
$y_{CO_2}$	99.2 mole%	$y_{CO_2}$	0.9833 mole%
$x_{CO_2}$	0.187 mole%	$x_{CO_2}$	0.06 mole%
pH	3.44	pH	3.60
CR	3.98 mm/y	CR	1.44 mm/y

Notice that the low-pressure case shows a higher corrosion rate value when compared to the high-pressure case. The reason why is because at higher pressure the intrinsic solubility of CO<sub>2</sub> decreases as the pressure increases. From the table, notice that more CO<sub>2</sub> is dissolved ( $x_{CO_2}$ ) in the aqueous phase at low pressure than at the high-pressure case.

## Chapter VI: Calculating corrosion rates using ScaleChem Objects

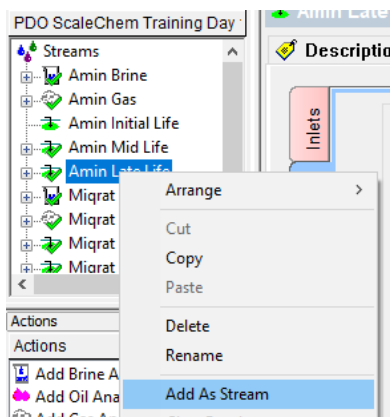
For this example, you need to have access to the **Amine Reservoir.oad** file. The main objective of this example is to learn how to set up a corrosion rate calculation using the results obtained in the ScaleChem tool.

In this example, the **Amine Late Life** reservoir results will be used to perform corrosion rate calculations.

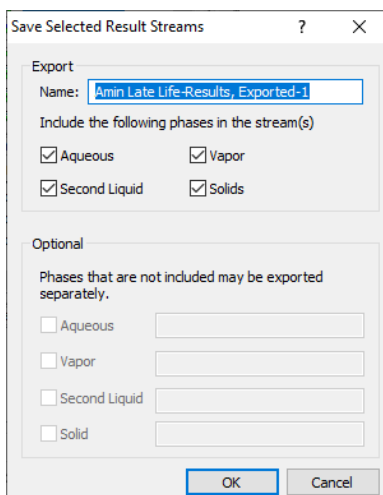
### Single Point Calculations

Corrosion rate calculations can be performed using streams. This means that we need to export the contents of the **Amine Late Life** reservoir into a stream. To do this, follow the steps below:

- ✓ Right click on the **Amine Late Life** ScaleChem Object and select the option **Add as Stream**



- ✓ This opens a new window. **Select** the phases of interest that you want to export, in this case we are going to select all the phases, since we want to export all the contents of the reservoir.
- ✓ Leave the default name and then click **OK**




- ✓ In the new exported stream, change the units from **concentration** (e.g., mg/L) to **moles**. Select **Metric | Batch | Moles**
- ✓ Change the Thermodynamic Framework to **AQ**
- ✓ Add a **Corrosion Rate** Calculation for CS 1018

**Important note:** If changes are made in the Brine Analysis and the Gas Analysis, there will be changes in the Saturator object. The chemistry for the corrosion rates needs to be updated manually following the steps given above.

- ✓ Rename the new corrosion rate calculation as **CS1018-CR**
- ✓ Go to the **Survey by** option and select **Single Point Rate**
- ✓ Change the **contact surface** to **carbon steel 1018**
- ✓ Click **OK** and then **Calculate**

## 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	155.000	3.06343	3.71742

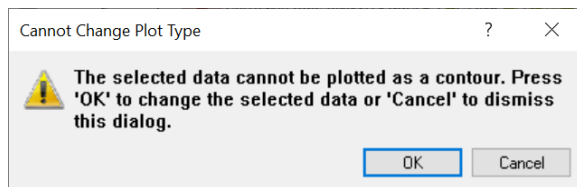
The predicted corrosion rate of carbon steel at 155 °C and 379 atm is ~3.06 mm/year.

## Survey Calculations

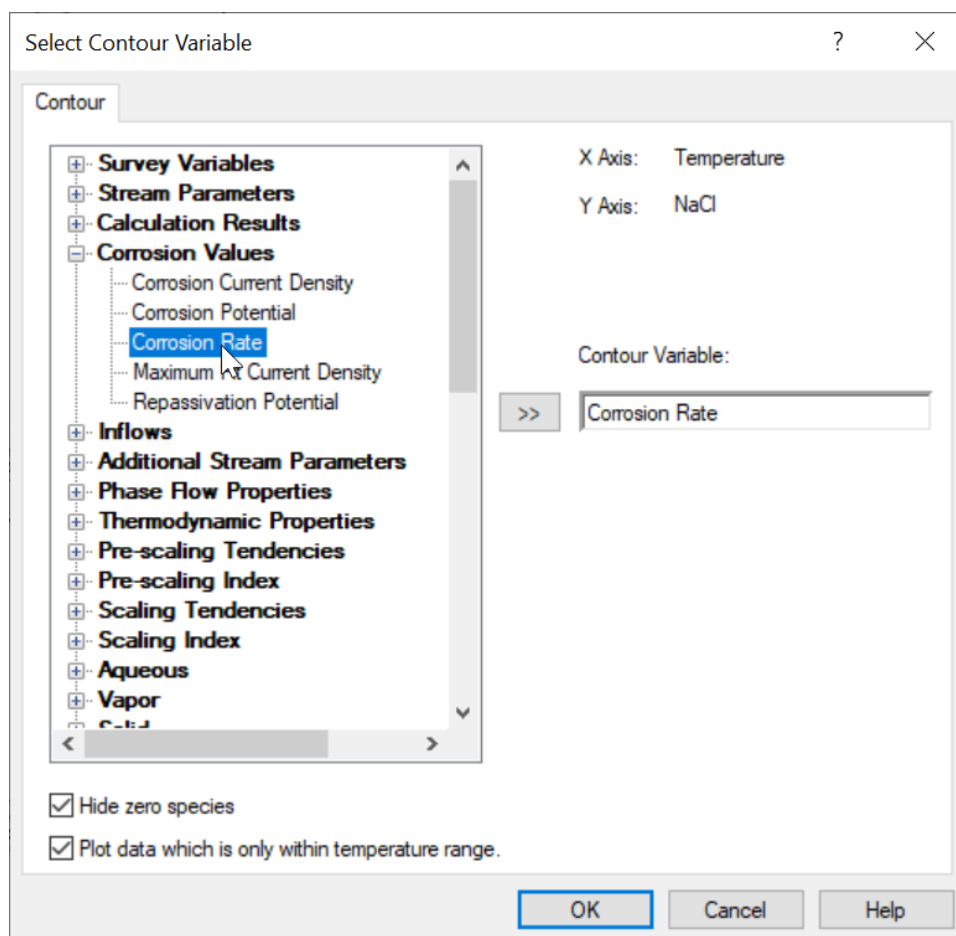
- ✓ Select the **Amin Late Life-Results, Exported** stream and add a **Survey by Temperature** and then by **Pressure**. This option will allow you to calculate the corrosion rate at a specified temperature and pressure range.
- ✓ Click on the **specs...** button next to the temperature option. This opens a new window.
- ✓ Under the **Survey Range** tab enter the following range:
  - a. Range: 25 – 155 °C
  - b. Number of steps: 20
- ✓ Select **Var.2 – Pressure** to specify the Pressure Range
- ✓ Under the **Survey Range** tab enter the following range:
  - a. Range: 20 – 385 atm
  - b. Number of steps: 20
- ✓ Click **OK** and then **Calculate**

## Analyzing the Results

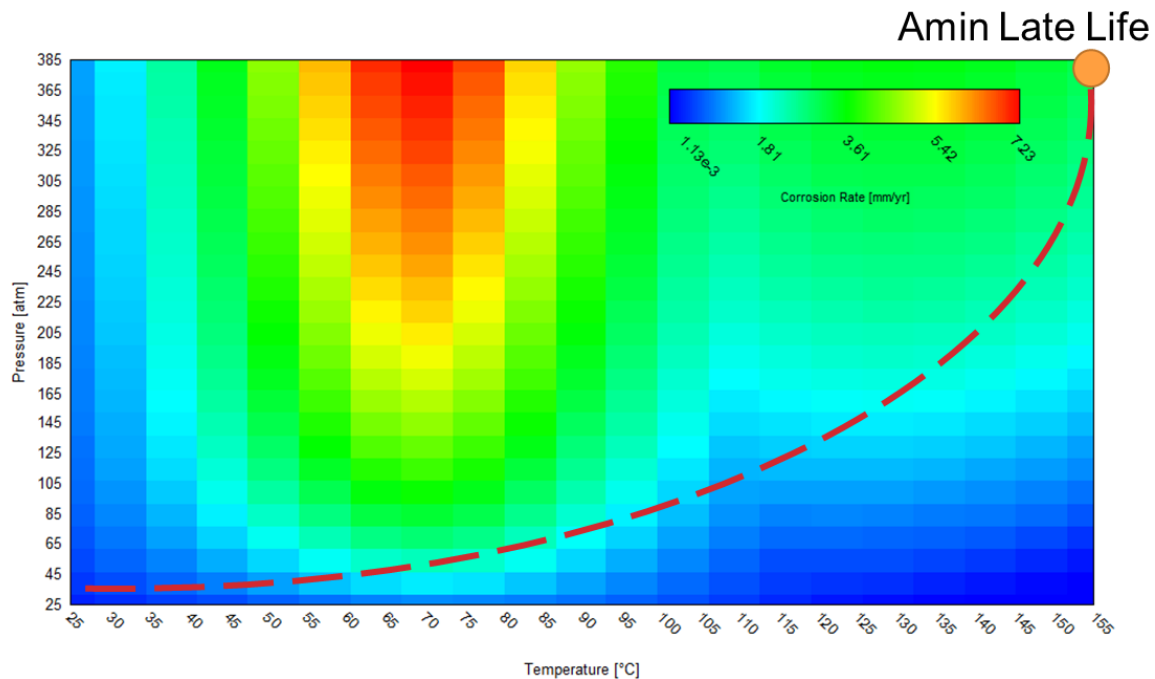
- ✓ Click on the **General Corr. Rate** tab (  General Corr. Rate ). This tab displays a plot showing the results of corrosion rate and pH as a function of temperature and concentration. This plot that is too hard to read. Fortunately, we have the option of creating a contour plot to visualize the results in a much better way.
- ✓ Click on the **Contour Plot** icon . An error message will appear. Click OK



- ✓ A new window appears asking you to select the contour variable of interest. Go to the **corrosion values** category and expand it. Select **Corrosion rate** by double clicking on it.



✓ Click OK



This contour diagram shows the effect of both temperature and pressure on the corrosion rate of Carbon Steel 1018. The highest corrosion rates are represented by the red color (7.23 mm/year) and the lowest corrosion rates are represented by the blue color (0.001 mm/year). If you were to overlap the production conditions (or T/P profile) onto this plot, you could get an idea of the corrosion rates of carbon steel at each location, starting from reservoir conditions going up to the surface.

✓ **Save** the file



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