

Chapter III – OLI Studio: Corrosion Analyzer

Corrosion Analyzer is a module within the OLI Studio. A separate license enables this module. Corrosion Analyzer is first-principles corrosion prediction tool. As in Stream Analyzer, for all calculations we will create one or more objects, referred to as a **Streams**, which are used to define a particular chemistry, temperature, and pressure.

There are two different types of calculations that can be carried out in Corrosion Analyzer: Corrosion Rates and Stability Diagrams (Potential vs pH and Potential vs species diagrams). A brief definition of each type of calculation is given below.



Stability Diagram is used to predict the stability of metals, metal ions, oxides, etc. as a function of T, P and solution composition. With this tool you can draw conclusions about the ranges of immunity to corrosion, possible passivation and dissolution of metals in the presence of species that promote or inhibit corrosion.



Corrosion Rates is used to predict the general corrosion rate, the propensity for localized corrosion (pitting or crevice corrosion) to occur, polarization curves, and heat treatment effects of metallic materials at one specific equilibrium state. The effects of temperature, pressure, pH, concentration of species, and velocity on corrosion are also included.

In this chapter several examples will be provided to cover these calculation types.

Section 7. Stability Diagrams

In this section you are going to learn how to set up a Stability Diagram and how to interpret the results when using this tool.

OLI Studio - [Document1*]

File Edit Streams Calculations Chemistry Tools View Window Help

Stream Parameters

Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5082
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Calculation Parameters	
Use Single Titrant	No
pH Acid Titrant	HCL
pH Base Titrant	NAOH
Inflows (mol)	
H2O	55.5082
Contact Surface	

Type of diagram
Pourbaix Diagram
Potential vs. Species

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: Evs pH
User-selected titrants
Enter the contact surface for this calculation in the contact surface section of the grid.

Alloy Activity Module:
Activated
Calculation not done

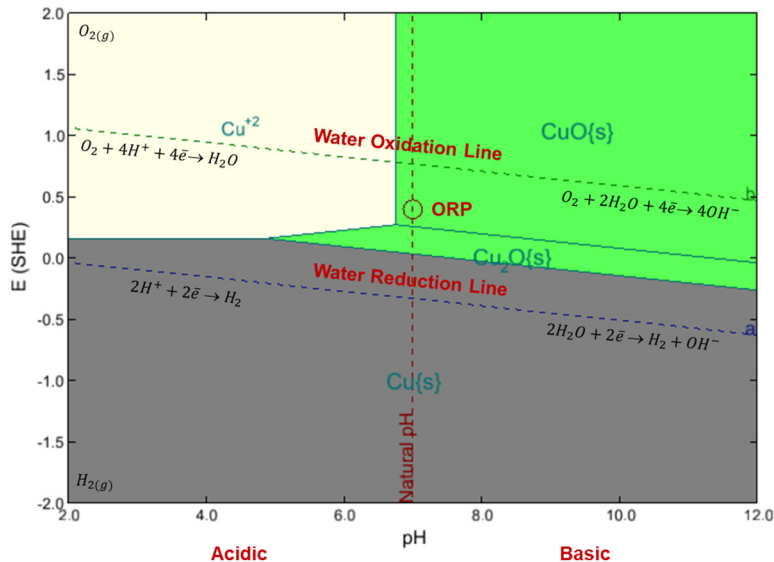
Advanced Search Add as Stream Export

For Help, press F1

How to Interpret a Stability Diagram

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.

A schematic representation of the Pourbaix diagram for copper in water at 25 °C and 1 atm is shown in the image below.



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

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 CuO and Cu₂O as the solid phases produced by oxidation of Cu.

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 plot above, Cu²⁺ is the ionic species that is the most stable.

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

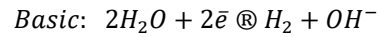
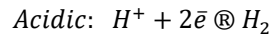
Below the water reduction line (a): Water decomposes to form H₂ gas. Above the water oxidation line (b): Water decomposes to form O₂ gas. The region within these lines (a and b) is called the stability region of water.

The lines that divide different species in the Pourbaix diagram show the equilibrium conditions. These lines represent the equilibrium for chemical and electrochemical reactions.

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

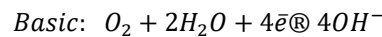
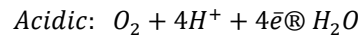
How to determine if corrosion in the absence of oxygen is possible?

In the absence of oxygen, the most common reduction reaction is the reduction of the proton to elemental hydrogen (as shown by line **a** in the plot below). Depending of the pH that reactions that can occur are the following:



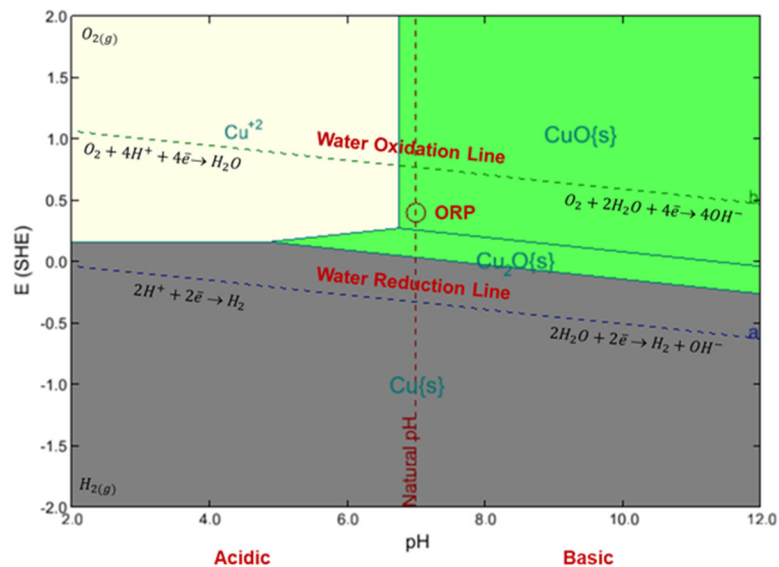
For a corrosion process to proceed, the line **a** must lie above a line that corresponds to an equilibrium between the metal and metal-containing ions.

In oxygen-containing solutions, O_2 can be reduced to H_2O (as shown by line **b**). Depending of the pH that reactions that can occur are the following:



For a corrosion process to occur, the line **b** must lie above a line that corresponds to an equilibrium between the metal and metal-containing ions.

Passivation is likely if **b** lies above a line that corresponds to an equilibrium between the metal and a sparingly soluble compound.



Stability diagram for Copper in Water at 25°C and 1 atm

Building a Pourbaix Diagram

Example 40: Pourbaix Diagram of Fe-H₂O System

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

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.

Stability Diagram Calculation			
Calculation Settings		Stream Composition and Conditions	
Stream Name	Fe-H ₂ O System	Stream Amount	Calculated
Name Style	Display Formula	Temperature	25 °C
Unit Set	Metric, Batch, Moles	Pressure	1 atm
Framework	AQ	pH Range	2-12
Calculation Type	Stability Diagram	H ₂ O	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*

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 **Stability Diagram** calculation or by selecting the **Chemical Diagram** icon in the Actions Pane.

The screenshot shows the OLI Studio interface for a 'Fe-H₂O System' calculation. The main window displays a table with the following data:

Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5082
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Inflows (mol)	
H ₂ O	55.5082

The 'Add Calculation' dropdown menu is open, showing options: Single Point, Survey, Chemical Diagram, **Stability Diagram** (highlighted), and Corrosion Rates. The 'Actions' pane on the left also has 'Add Stability Diagram' highlighted.

Select **Pourbaix Diagram** as Type of Survey – Default

Click on the new *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 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 need it to create the Pourbaix Diagram. This option will enable the different oxidation states of the selected metal.

OLI Studio - [Stability Diagrams.oad*]

File Edit Streams Calculations Chemistry Tools View Window Help

Navigator

Document1*

Stability Diagrams.oad*

Streams

- Fe-H2O System
 - Fe-H2O Pourbaix Diagram

Actions

Plot Template Manager

Save

Fe-H2O Pourbaix Diagram

Description Definition Stability Diagram Report

Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5082
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Calculation Parameters	
Use Single Titrant	No
pH Acid Titrant	HCL
pH Base Titrant	NAOH
Inflows (mol)	
H2O	55.5082
Contact Surface	

Type of diagram: Pourbaix Diagram

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

User-selected titrants

Enter the contact surface for this calculation in the contact surface section of the grid.

Alloy Activity Module: Activated

Calculation not done

Advanced Search Add as Stream Export

For Help, press F1

Leave the default titrants for this calculation: HCl and NaOH

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

Note: You also have the option to use the drop-down arrow to search for the metal or alloy of interest.

OLI Studio - [Stability Diagrams.oad*]

File Edit Streams Calculations Chemistry Tools View Window Help

Navigator

Document1*

Stability Diagrams.oad*

Streams

Fe-H2O System

Fe-H2O Pourbaix Diagram

Actions

Actions

Plot Template Manager

Save

Fe-H2O Pourbaix Diagram

Description Definition Stability Diagram Report

Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5082
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Calculation Parameters	
Use Single Titrant	No
pH Acid Titrant	HCL
pH Base Titrant	NAOH
Inflows (mol)	
H2O	55.5082
Contact Surface	
Fe	
Display Name	OLI Name
OLI F2	F2
F2	F2
Fe	FEEL
OLI FEEL	FEEL
SYN Flowers of sulphur	SULFUREL
SYN Fluorine	F2

Input

Advanced Search Add as Stream Export

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

User-selected titrants

Enter the contact surface for this calculation in the contact surface section of the grid.

Alloy Activity Module:

Activated

Calculation not done

For Help, press F1

NUM

At this point all the basic inputs to create a Pourbaix Diagram have been defined. Notice that in the summary box the following default plotting settings have been defined: Potential range: -2 to 2 V vs SHE and pH range: 0-14. You can modify these default values before running the calculation.

The screenshot shows the OLI Studio interface for creating a Pourbaix Diagram. The main configuration table is as follows:

Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5082
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Calculation Parameters	
Use Single Titrant	No
pH Acid Titrant	HCl
pH Base Titrant	NaOH
Inflows (mol)	
H2O	55.5082
HCl	0.0
NaOH	0.0
Fe	0.0
Contact Surface (mol)	
Fe	

The Summary panel on the right shows the following settings:

- Type of diagram: Pourbaix Diagram
- 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: HCl, Base: NaOH
- Range on E: -2.00000 to 2.00000 V (SHE)
- Range on pH: 0.0 to 12.00000
- Subsystems: Iron, Water
- Alloy Activity Module: Activated
- Calculation not done

Click on the **Specs** button. This will open the **Stability Diagram Options** Window

Under the **Display** Category you will see the **Display Choices** tab. Under this tab make sure to select the following options:

No Aqueous lines

Show natural pH

Show ORP

Under **Display Subsystems** check the **Iron** and **Water** boxes

Under **Shading** select the option **Shade Subsystem** and select **Iron**.

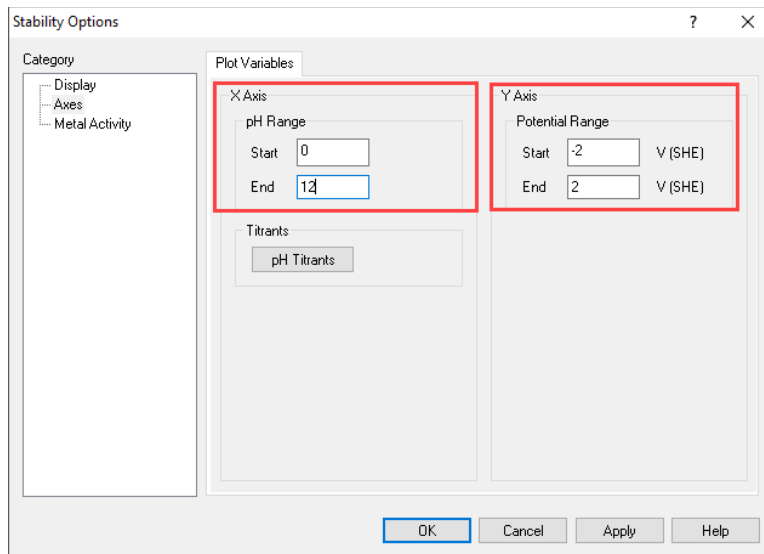
Click **OK** to close the window

The screenshot shows the OLI Studio interface with a Fe-H2O Pourbaix Diagram. The 'Stability Options' dialog box is open, showing the 'Display Choices' tab. The 'Display' category is selected. Under 'Aqueous and Solid Lines', the 'No Aqueous lines' radio button is selected. Under 'Shading', the 'Shade subsystem:' radio button is selected, and 'Iron' is chosen in the list. Under 'Display Subsystems', the 'Iron' and 'Water' checkboxes are checked. The 'OK' button is highlighted. The background shows the Pourbaix Diagram with a table of parameters:

Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5082
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Calculation Parameters	
Use Single Titrant	No

Click on the **Axes** Category. This will show you the Plot Variables tab.

Note: In the **Axes** Category you can modify the axes of the Pourbaix Diagram and change the default titrants.



Change the X Axis or pH range to 2-12


Leave the default values for the Y Axis of Potential Range (-2 to 2 V SHE)

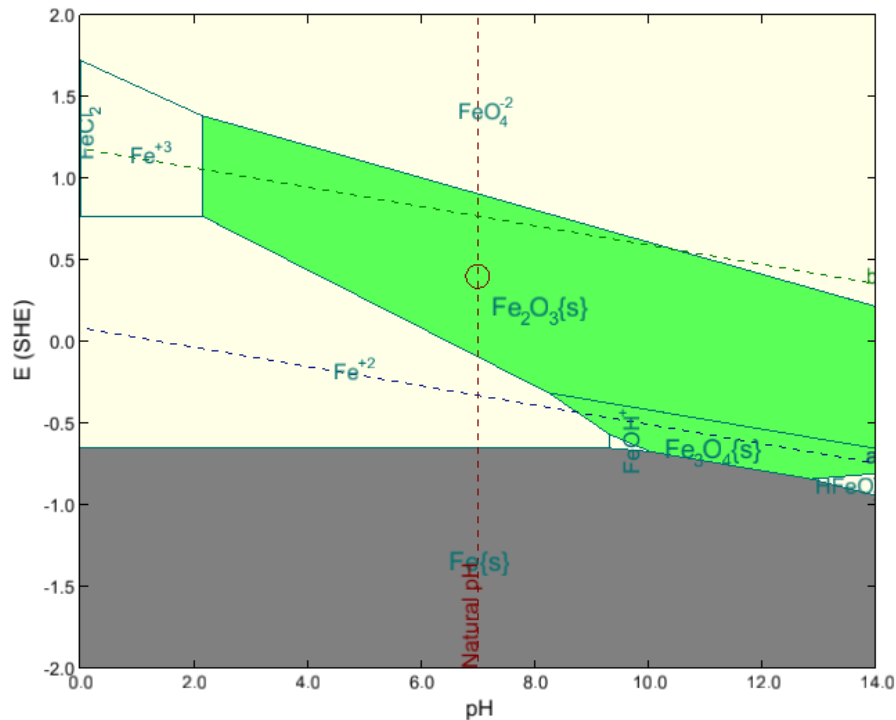
Click **OK** to close the window

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 and name it as *Stability Diagrams*.

Analyzing the Results

Click on the **Chemical Diagram** tab ( **Stability Diagram**). This tab displays the Pourbaix Diagram for the Fe-H₂O system at 25 °C and 1 atm.



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⁺². 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 Fe₃O₄ (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 Fe₂O₃ (hematite). Hematite is the dehydrated form of Fe(OH)₃ and Fe₃O₄, 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 white sections of the plot represent the dominant iron-containing species dissolved in solution. The species with the largest range is 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 Fe₂O₃ (hematite) is the most stable species that forms.

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

Selective Oxidation and Reduction Chemistry

Occasionally you may want to remove a specific oxidation state for an element when building a Stability Diagram. There are a variety of reasons to perform such an activity, one being that a specific oxidation state may be kinetically unavailable for the reaction. Another case is that perhaps you need to compare and contrast two systems. We will explore how to do this in the following example.

Example 41: Turning off the Fe^{+6} oxidation state in the Stability Diagram

In this example you will create a Stability diagram for iron in water at ambient conditions (see previous example for details on how to create this stream), learn how to change the default titrants and turn off/on different specific oxidation states of the metal of interest.

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.

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	H2SO4	0 moles
		NaOH	0 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 **Add Stability Diagram** icon in the Actions Pane.

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. **Add** H2SO4 and NaOH as inflows. **Note:** H2SO4 and NaOH will be used as titrants to adjust pH

Select **Pourbaix Diagram** as Type of Survey – Default

Click on the new *Stability Diagram* and press **<F2>** to change the name to *Fe-H2O Selective Oxidation*

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

Changing the Default Titrant

In the **Calculation Parameters** grid, **click** on HCL (which is default titrant). A drop-down arrow appears, **click** on it and **select** H2SO4. NaOH has been selected by default.

Calculation Parameters	
Use Single Titrant	No
pH Acid Titrant	HCL
pH Base Titrant	H2O
Inflows	
H2O	H2SO4
H2SO4	HCL
	NAOH

Note: You can also change the default titrant using the **Specs** button

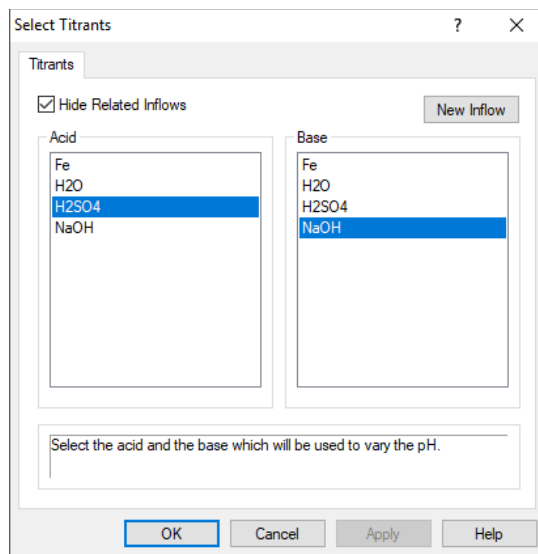
Click on the **Specs** button

Select the **Axes** option under the **Category** window

Click on **pH Titrants**. This will open a new window

The screenshot shows the OLI Studio interface for a 'Fe-H2O Selective Oxidation' simulation. The 'Calculation Parameters' grid is visible, showing 'pH Acid Titrant' set to 'HCL' and 'pH Base Titrant' set to 'H2O'. The 'Stability Options' dialog box is open, showing the 'Category' window with 'Axes' selected, and the 'pH Titrants' window with 'pH Titrants' selected. Red boxes and numbers 1, 2, and 3 highlight the 'Specs...' button, the 'Axes' option, and the 'pH Titrants' option respectively.

Select H2SO4 as the **Acid** titrant, and **NaOH** as the **Base** titrant. Then **click** **OK** to exit both windows.




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

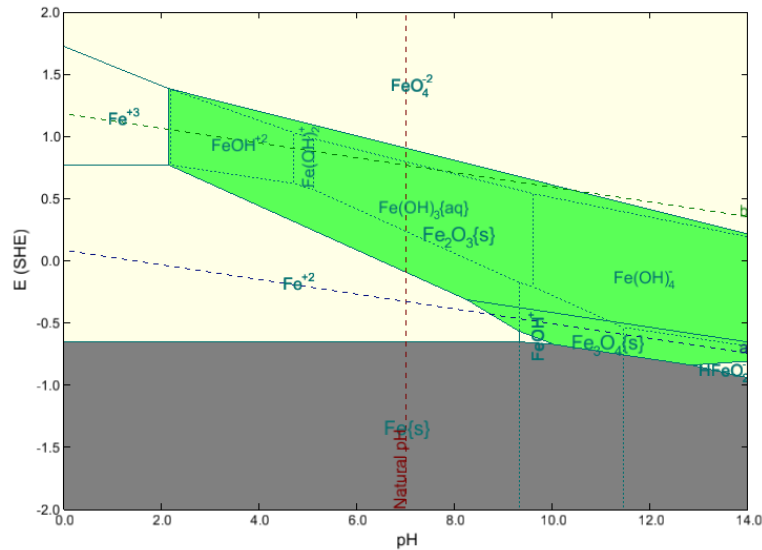
Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5082
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Calculation Parameters	
Use Single Titrant	No
pH Acid Titrant	H2SO4
pH Base Titrant	NAOH
Inflows (mol)	
H2O	55.5082
H2SO4	0.0
Fe	0.0
Contact Surface (mol)	
Fe	

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-H₂O system at 25 °C and 1 atm.



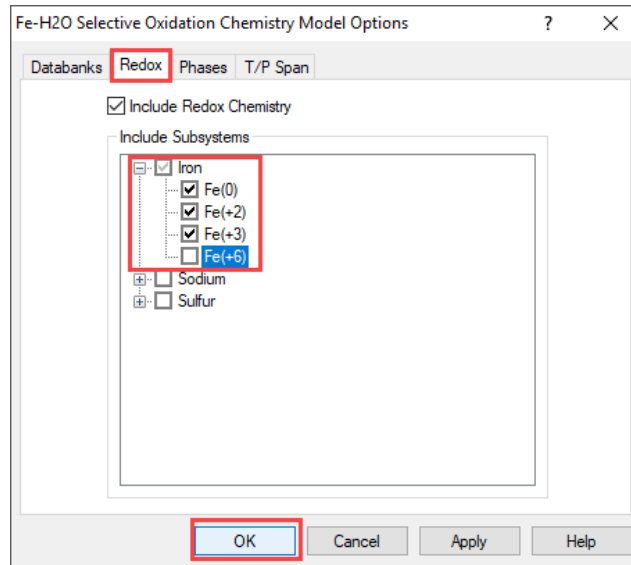
Marcell Pourbaix did not consider the FeO_4^{2-} ion in his work. This is iron in the +6 oxidation state for which there was little thermodynamic data available in the 1960s. To reproduce his work, we need to remove the redox subsystem that pertains to Fe(+6).

Selective Redox, removing an undesired oxidation state

In the Menu bar go to **Chemistry > Model Options**. This will open a new window

The screenshot shows the OLI Studio interface. The 'Chemistry' menu is open, and 'Model Options...' is selected. The background displays the Pourbaix Diagram for the Fe-H₂O system, showing the stability regions for various iron species. The diagram is titled '0.02177 pH, 1.647 V (SHE)'. The y-axis is E (SHE) ranging from -1.0 to 2.0, and the x-axis is pH ranging from 0.0 to 14.0. The diagram shows stability regions for various iron species: Fe⁺³, FeOH⁺², Fe(OH)₃, Fe(OH)₃(aq), Fe₂O₃(s), Fe(OH)₄, Fe⁺², Fe(s), FeO₄⁻², Fe(OH)₂, Fe₂O₃(s), Fe(OH)₄, Fe(OH)₂, Fe₂O₃(s), and HFeO₂. A vertical dashed line at pH ≈ 7.2 is labeled 'Natural pH'.

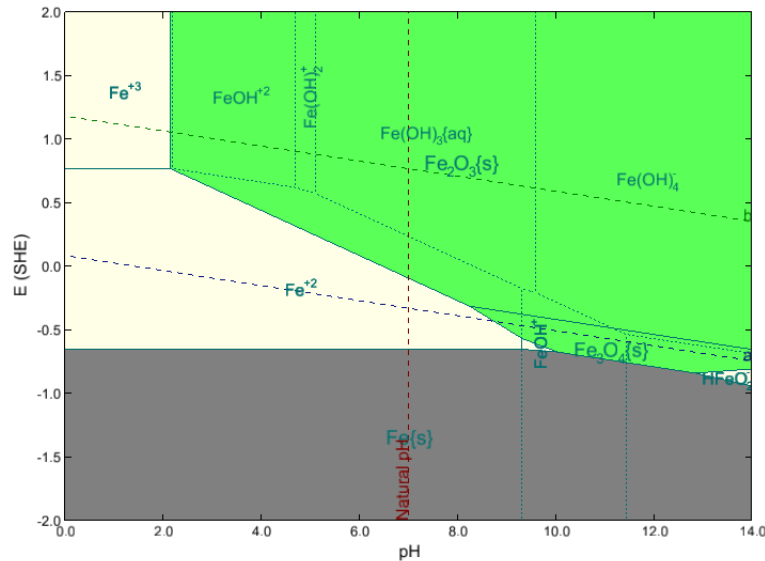
Select the **Redox** tab, expand the Iron Subsystems by clicking on the '+' icon, and **uncheck** the **Fe(+6)** oxidation state. Note that if you have an inflow component with this oxidation state it will remain in the calculation. Click the **OK** button to save your changes and close the window.



We are ready to recalculate to consider the changes. Press the **<F9>** key or go to the **Definition** tab and click on the **Calculate** button.

Analyzing the Results

Click on the **Chemical Diagram** tab (Stability Diagram). In the figure below, you can see that the region dominated by the FeO_4^{2-} ion is not present.



Modeling the Effects of Hydrogen Sulfide on Corrosion

Example 42: The Effect of Hydrogen Sulfide on the Corrosion of Iron

The H_2S (S^{2-}) forms a relatively insoluble precipitate with 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.

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.

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 **Add Stability Diagram** icon in the Actions Pane.

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. **Add 1e-4 moles of H2S** as an inflow.

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*

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

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

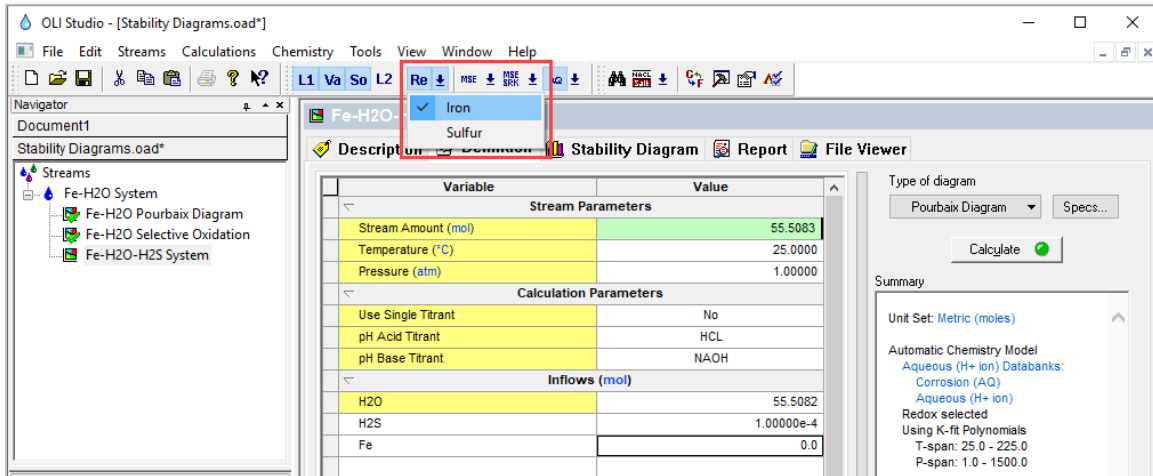
The screenshot shows the OLI Studio interface for a 'Fe-H2O-H2S System'. The main window displays a table of variables and values:

Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5083
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Calculation Parameters	
Use Single Titrant	No
pH Acid Titrant	HCL
pH Base Titrant	NAOH
Inflows (mol)	
H2O	55.5082
H2S	1.00000e-4
Fe	0.0
Contact Surface (mol)	
Fe	

On the right side, the 'Type of diagram' is set to 'Pourbaix Diagram'. The 'Summary' section shows the unit set as 'Metric (moles)' and the automatic chemistry model settings, including 'Aqueous (H+ ion) Databanks: Corrosion (AQ) Aqueous (H+ ion)', 'Redox selected', and 'Using K-fit Polynomials'.

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.

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

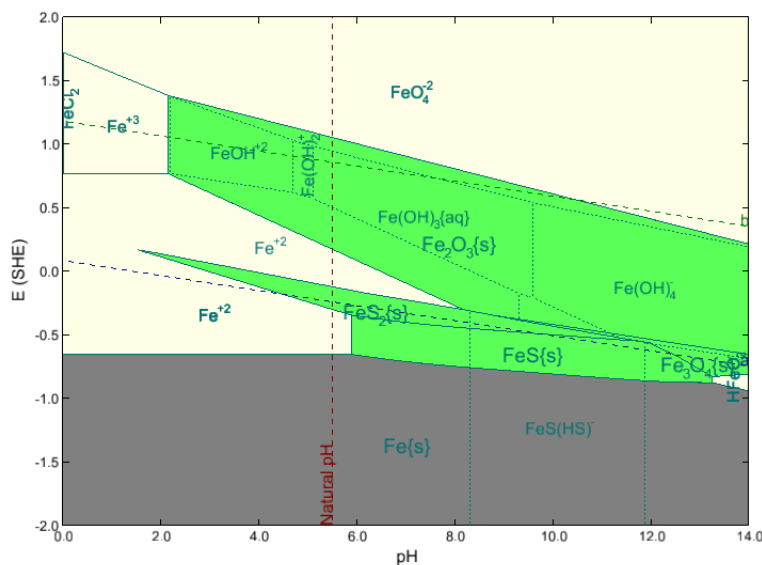


We are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key

It is time to **save** your file (**File > Save as...**) or using the **save** icon in the tool bar. You can save it under the same file created in the previous example named *Stability Diagrams*.

Analyzing the Results

Click on the **Chemical Diagram** tab (Stability Diagram). This tab displays the Pourbaix Diagram for the Fe-H2O-H2S system at 25 °C and 1 atm.



Inspection of the diagram reveals a profound effect of H₂S on the corrosion of iron. New stability fields of FeS and FeS₂ 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⁺ reduction line (a), a process consisting of the reduction of H⁺ to H⁰ and oxidation of Fe to FeS is likely to occur in de-aerated environments. FeS forms a passive film and offers some protection against corrosion.

In fact, the protection due to the formation of FeS is possible over a much wider pH range than that due to the formation of Fe₃O₄ (magnetite) in the absence of H₂S.

This has important implications for corrosion in refinery installations, where H₂S is frequently present.

Modeling Corrosion at High Temperature

Example 43: High Temperature Iron in Water

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.

Stability Diagram Calculation			
Calculation Settings		Stream Composition and Conditions	
Stream Name	Fe-H2O System	Stream Amount	Calculated
Name Style	Display Formula	Temperature	300 °C
Unit Set	Metric, Batch, Moles	Pressure	150 atm
Framework	AQ	pH Range	0-14 (Default)
Calculation Type	Stability Diagram	H2O	55.5082 moles
Contact Surface	Fe		

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 **Add Stability Diagram** icon in the Actions Pane.

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

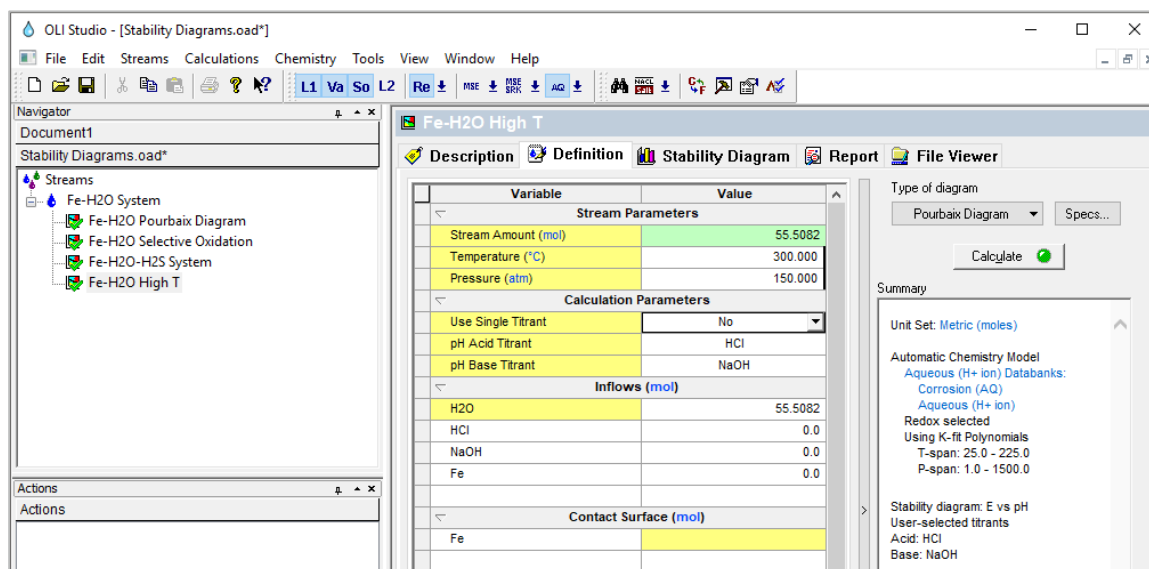
Enter the composition, temperature and pressure of the stream given in the table above

Select **Pourbaix Diagram** as Type of Survey – Default

Click on the new *Stability Diagram* and press **<F2>** to change the name to *Fe-H2O High T*

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


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

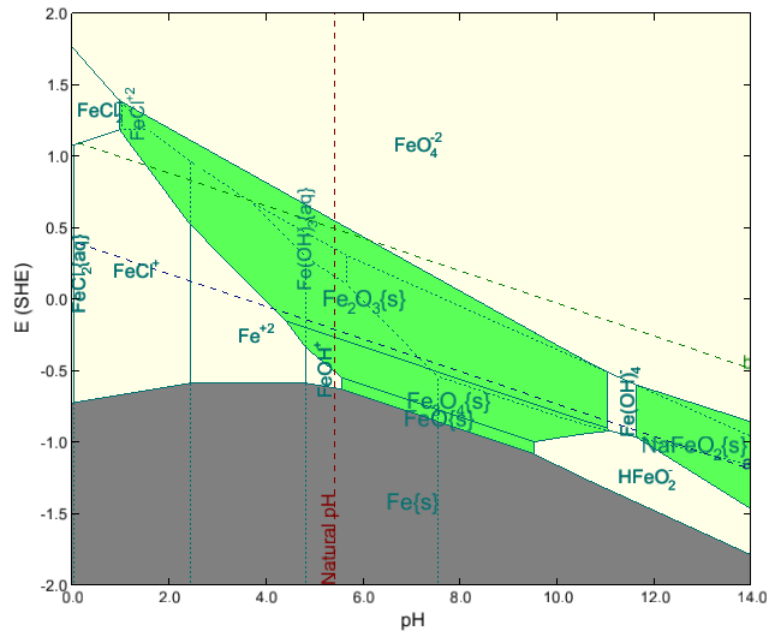


We are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key

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-H₂O system at 300 °C and 150 atm.



We can see from the diagram above that passivation is only possible at moderate pH's.

Example 44: Neutralization of Refinery Streams with Alkanolamines

In this example you will create a stability diagram for alkaline neutralization in an oil refinery.

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.

Stability Diagram Calculation			
Calculation Settings		Stream Composition and Conditions	
Stream Name	Fe-H2O System	Stream Amount	Calculated
Name Style	Display Formula	Temperature	50 °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	HCl	0 moles (Acid Titrant)
		DEA ⁹	0 moles (Base Titrant)
		C8H18	2E-07 moles
		C7H16	8E-07 moles
		C3H8	1.2E-04 moles
		C4H10	2E-05 moles
		C5H12	7E-6 moles
		C6H14	2E-6 moles
		H2S	0.01 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 **Add Stability Diagram** icon in the Actions Pane

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

Select **Pourbaix Diagram** as Type of Survey – Default

Click on the new *Stability Diagram* and press **<F2>** to change the name to *Fe-H2O-Alkanoamines*

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

Change the **Base Titrant** to **DEA**

Turn Redox ON for Sulfur. **Click** on the drop-down arrow next to the **Re** button and select **Sulfur**

Note: You can also enable Redox reactions via the menu bar: **Chemistry > Model Options > Redox** tab.

Make sure that Sulfur is checked.

⁹ The "ESP" name for this species is DEXH, which can be used as an input to make your life easier. The formula name is: HN(C2H4OH)2

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

The screenshot displays the OLI Studio interface for setting up a Pourbaix Diagram. The 'Re' menu is open, showing 'Iron' selected. The 'Stream Parameters' table is as follows:

Parameter	Value
Stream Amount (mol)	55.5184
Temperature (°C)	50.0000
Pressure (atm)	1.00000

The 'Calculation Parameters' table is as follows:

Parameter	Value
Use Single Titrant	No
pH Acid Titrant	HCl
pH Base Titrant	HN(C2H4OH)2

The 'Inflows (mol)' table is as follows:

Species	Value
H2O	55.5082
HCl	0.0
HN(C2H4OH)2	0.0
C8H18	2.00000e-7
C7H16	8.00000e-7
C3H8	1.20000e-4
n-C4H10	2.00000e-5
C5H12	7.00000e-6
C6H14	2.00000e-6
H2S	0.0100000
NaOH	0.0
Fe	0.0

The 'Contact Surface (mol)' table is as follows:


Species	Value
Fe	

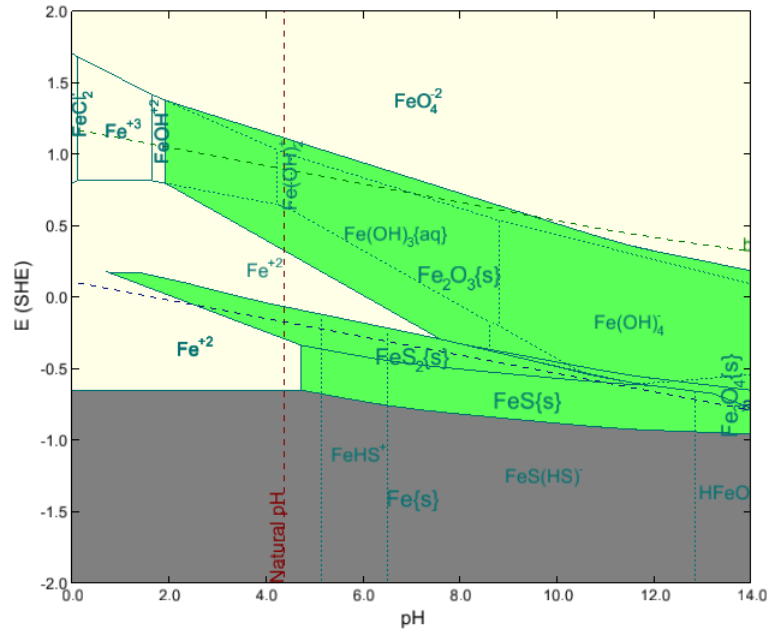
The 'Summary' panel on the right shows the diagram type as 'Pourbaix Diagram' and the calculation status as 'Calculation not done'.

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-H₂O system at 50 °C and 1 atm.



Modeling the Effects of Complexation on Corrosion

In this section we will simulate the reaction of Copper with Ammonia and Gold metal with Cyanide. This section attempts to answer the question of how strong complexing agents affect the passivation of these metals.

Example 45: Copper and Ammonia

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.

Stability Diagram Calculation			
Calculation Settings		Stream Composition and Conditions	
Stream Name	Cu-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	Cu	NH3	0 moles

Add a new **Stream**

Click on the new Stream and press **<F2>** to change the name to *Cu-H2O System*

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

Under the *Cu-H2O System* Stream add a new Stability Diagram calculation. Go to the **Add Calculation** button

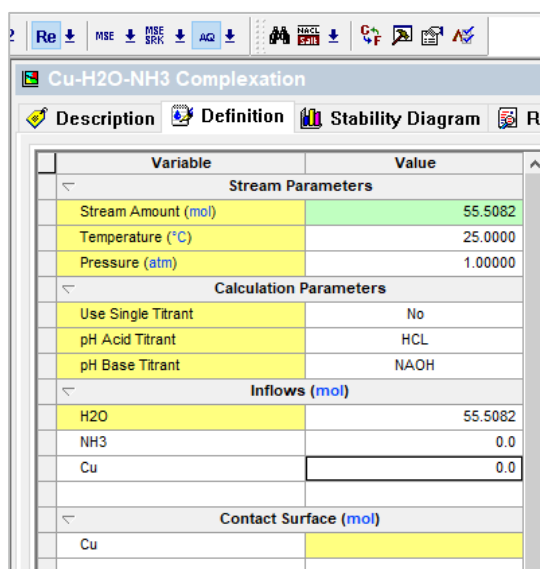
and select **Stability Diagram** calculation or by selecting the **Chemical Diagram** icon in the Actions Pane

Select **Pourbaix Diagram** as Type of Survey – Default

Click on the new *Stability Diagram* and press **<F2>** to change the name to *Cu-H2O-NH3*

Under the **Contact Surface** grid type **Cu**


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

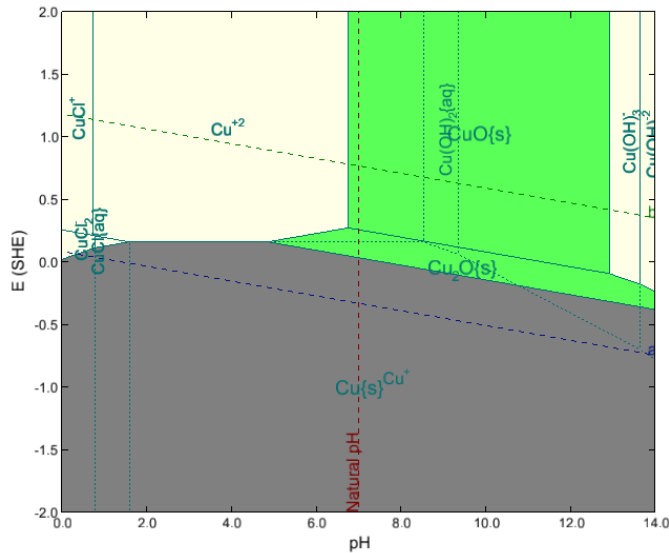


Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5082
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Calculation Parameters	
Use Single Titrant	No
pH Acid Titrant	HCL
pH Base Titrant	NAOH
Inflows (mol)	
H2O	55.5082
NH3	0.0
Cu	0.0
Contact Surface (mol)	
Cu	

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 Cu-H₂O system at 25 °C and 1 atm.



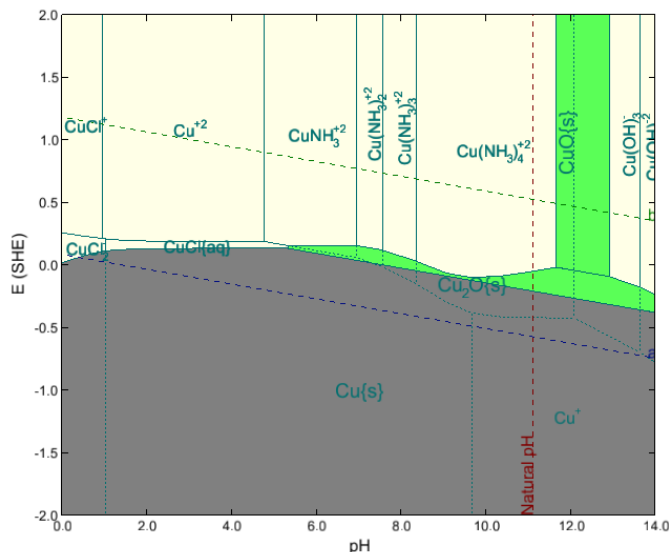
In the absence of oxygen (looking at only the **a** line), we can see that the copper equilibrium line lays above the hydrogen **a** line. This means there is insufficient oxidizing power in the water to corrode copper metal in pure water.


What happens if Ammonia (NH₃) is added to the solution? The next step is to understand the effect of NH₃ on the stability of copper.

Effect of NH₃ on the Stability of Copper

Go to the **Definition** tab, and change the amount of NH₃ from 0 to 0.1 moles
Click on the **Calculate** button or press the **<F9>** key

Analyzing the Results



Click on the **Chemical Diagram** tab ( **Stability Diagram**). This tab displays the Pourbaix Diagram for the Cu-H₂O-NH₃ system at 25 °C and 1 atm in a 0.1 m of NH₃ solution.

Notice that a large area of corrosive liquid has appeared in the stability field for the copper oxides. This means that it is thermodynamically possible for the ammonia to break down the passivation layer of copper oxide in the presence of oxygen. Notice that


in the absence of oxygen (the **a** line only), copper is still stable.

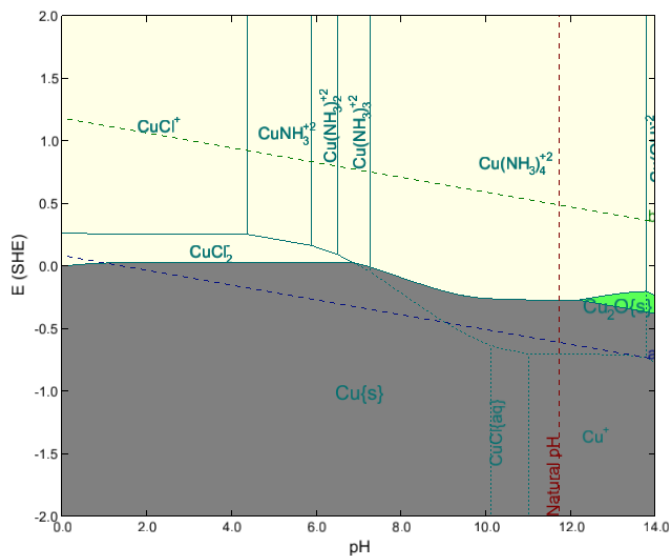
Now repeat the exercise with **1.5 moles of NH3**

Go to the **Definition** tab, and change the amount of NH3 from 0 to 1.5 moles

Click on the **Calculate** button or press the **<F9>** key

Analyzing the Results

Click on the **Chemical Diagram** tab ( **Stability Diagram**). This tab displays the Pourbaix Diagram for the Cu-H2O-NH3 system at 25 °C and 1 atm in a 1.5 m of NH3 solution.



At this concentration of ammonia, most, if not all the passivating copper oxide has been reacted away. Only at very high pH values are there any stable oxides.

Example 46: Gold in the presence of Cyanides

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.

Stability Diagram Calculation			
Calculation Settings		Stream Composition and Conditions	
Stream Name	Au-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	Au	NaCN	0 moles

Add a new **Stream**

Click on the new Stream and press **<F2>** to change the name to *Au-H2O System*

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

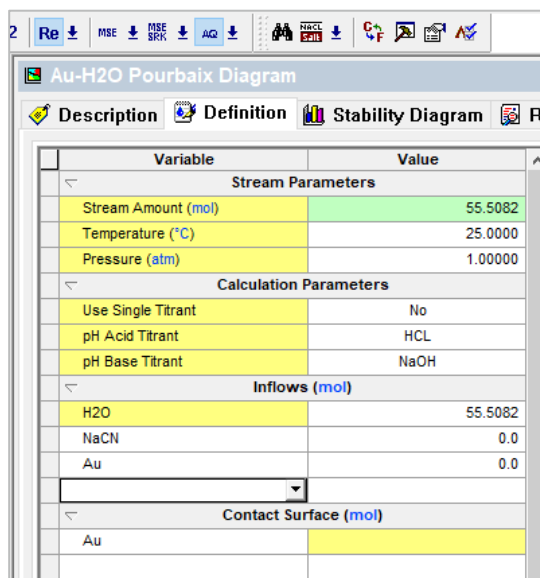
Under the *Au-H2O System* Stream add a new Stability Diagram calculation. Go to the **Add Calculation** button and select **Stability Diagram** calculation or by selecting the **Chemical Diagram** icon in the Actions Pane

Select **Pourbaix Diagram** as Type of Survey – Default

Click on the new *Stability Diagram* and press **<F2>** to change the name to *Au-H2O*

Under the **Contact Surface** grid type **Au**


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

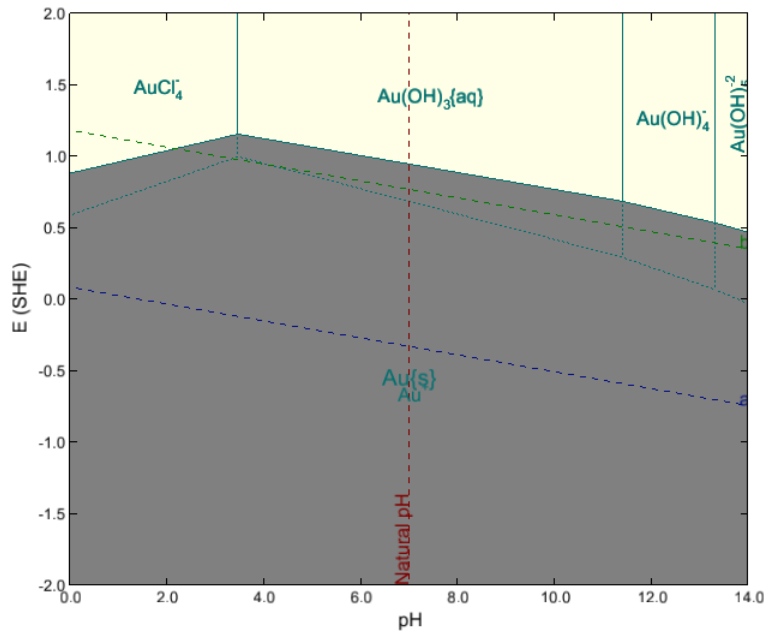


We are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key

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 Au-H₂O system at 25 °C and 1 atm.



You can see that without oxygen, gold metal is immune to corrosion. The hydrogen line **a** is below the gold equilibrium line. In the presence of oxygen, gold is still immune to corrosion except at very low pH.


One of the most commonly used leaching processes for **gold extraction** is the **cyanidation** process. This process is a hydrometallurgical technique for extracting gold from low-grade ores by converting the gold to a water-soluble coordination complex. Basically, this approach adds cyanide salts to water. We are going to simulate this using the software.

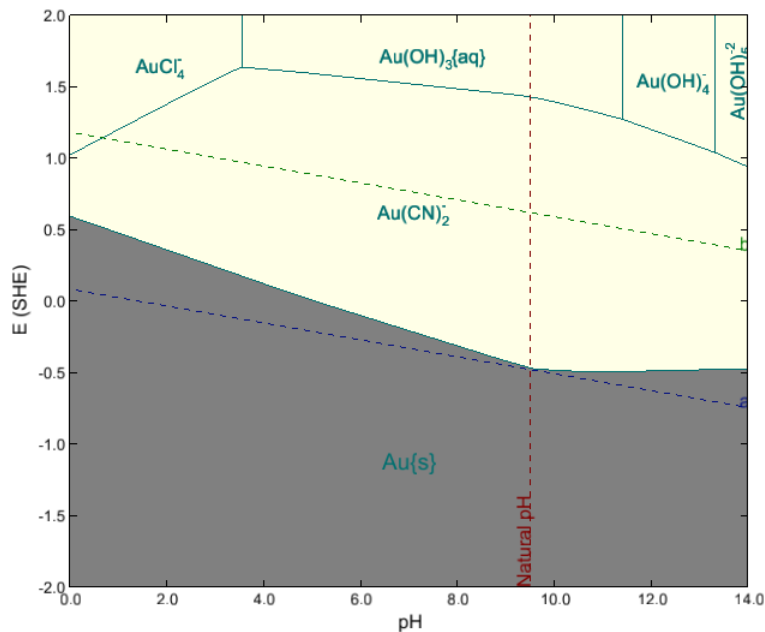
Effect of Cyanide on the Stability of Gold

Go to the **Definition** tab, and change the amount of NaCN from 0 to 1e-4 moles

Click on the **Calculate** button or press the **<F9>** key

Analyzing the Results

Click on the **Chemical Diagram** tab ( **Stability Diagram**). This tab displays the Pourbaix Diagram for the Au-H₂O-NaCN system at 25 °C and 1 atm.



In the presence of oxygen, gold completely corrodes with cyanide. This is primarily due to the formation of the gold complex: $Au(CN)_2^-$. This complex is stable over all regions where water is also stable. This means that now gold can be processed in water in a variety of conditions.

Modeling the Effect of Oxidizing Inhibitors on Corrosion

In this chapter we will look at the effect of modeling corrosion inhibitors. We will do this by superimposing two stability diagrams over one another. If one solid field overlaps the corrosion range of the other system, then passivation is likely.

Example 47: Iron in the presence of chromates

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.

Stability Diagram Calculation			
Calculation Settings		Stream Composition and Conditions	
Stream Name	Inhibitors	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		
Contact Surface	Cr		

Add a new **Stream**

Click on the new Stream and press **<F2>** to change the name to *Inhibitors*

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

Under the *Inhibitors* Stream add a new Stability Diagram calculation. Go to the **Add Calculation** button and select **Stability Diagram** calculation or by selecting the **Chemical Diagram** icon in the Actions Pane

Select **Pourbaix Diagram** as Type of Survey – Default

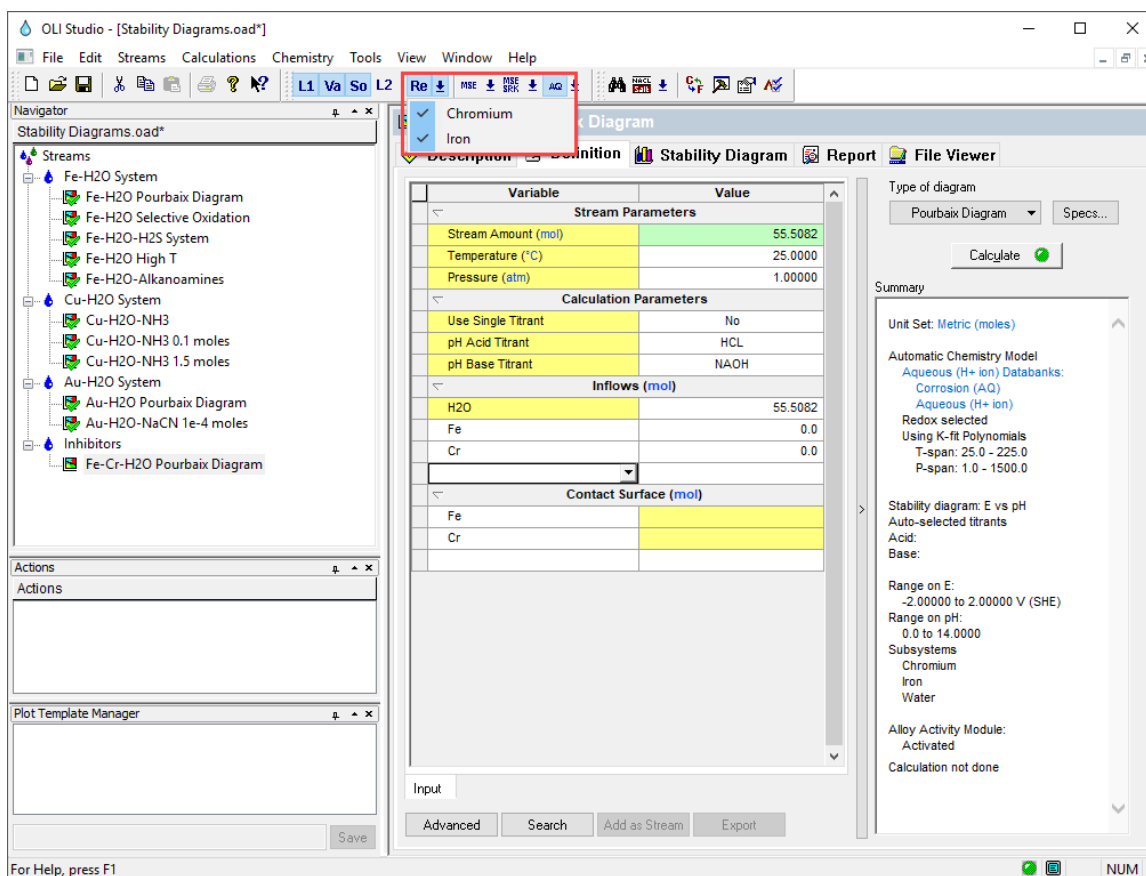
Click on the new *Stability Diagram* and press **<F2>** to change the name to *Fe-Cr-H2O Pourbaix Diagram*

Under the **Contact Surface** grid type **Fe** and then **Cr**

Note: Make sure that both **Fe** and **Cr** are enabled for Redox reactions. Use the arrow next to the **Re** button to expand the list.

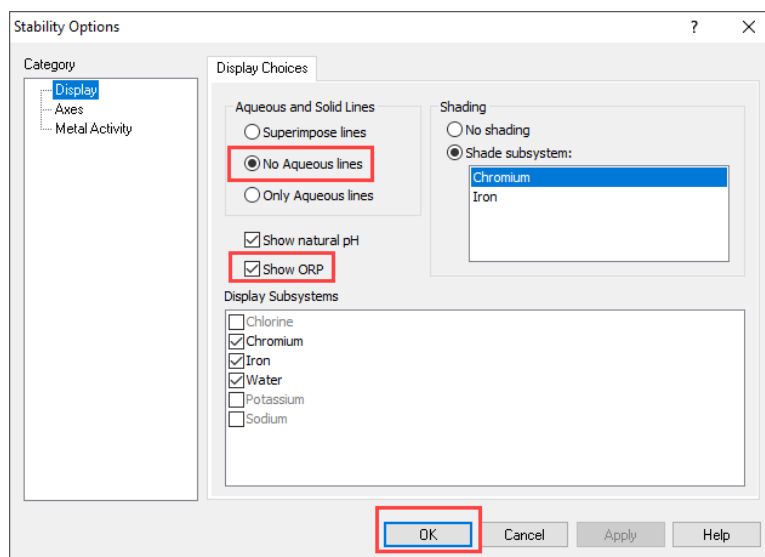
You can also enable Redox reactions via the menu bar: **Chemistry > Model Options > Redox** tab. Make sure that Fe and Cr boxes are checked.

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



Click the **Specs** button and under the Display Choices tab check the following options:

- No aqueous lines
- Show ORP




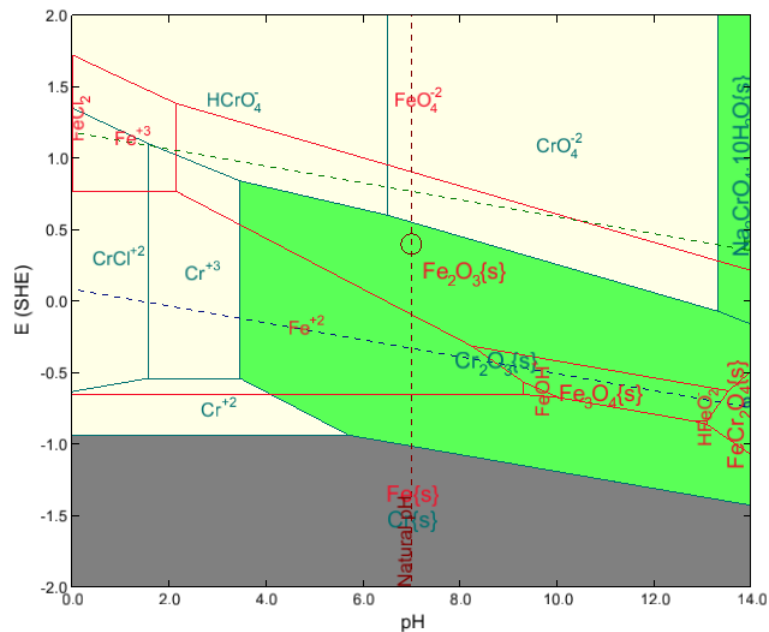
Click **OK** to close the Stability Options window

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-Cr-H₂O system at 25 °C and 1 atm.



As you can see in this diagram, the shaded chrome passivating solid ($\text{Cr(OH)}_{3\text{ppt}}$) overlays the corrosive region of the iron system. This means that there is potential for passivating the metal in that region.

The Cr(OH)_3 field overlaps with the corrosion range of Fe in most of the pH range. This causes inhibition because of the coupling of: Oxidation of Fe to Fe^{2+} , reduction of chromates to Cr(OH)_3 , and the deposition of a protective layer of Cr(OH)_3 .

Example 48: Iron in the presence of arsenates

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.

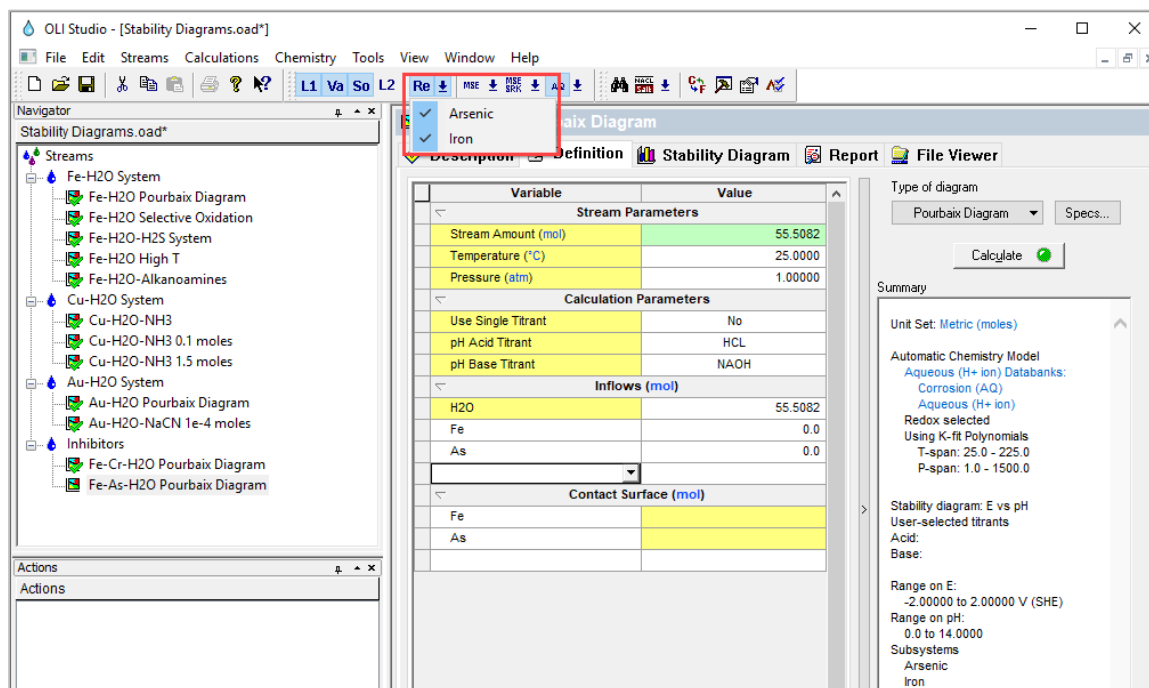
Stability Diagram Calculation			
Calculation Settings		Stream Composition and Conditions	
Stream Name	Inhibitors	Stream Amount	Calculated
Name Style	Display Formula	Temperature	25 °C
Unit Set	Metric, Batch, Moles	Pressure	1 atm
Framework	AQ	pH Range	0-14 (Default)
Calculation Type	Stability Diagram	H2O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

Under the *Inhibitors* Stream add a new Stability Diagram calculation. Go to the **Add Calculation** button and select **Stability Diagram** calculation or by selecting the **Chemical 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-As-H2O Pourbaix Diagram*. Under the **Contact Surface** grid type **Fe** and then **As**.

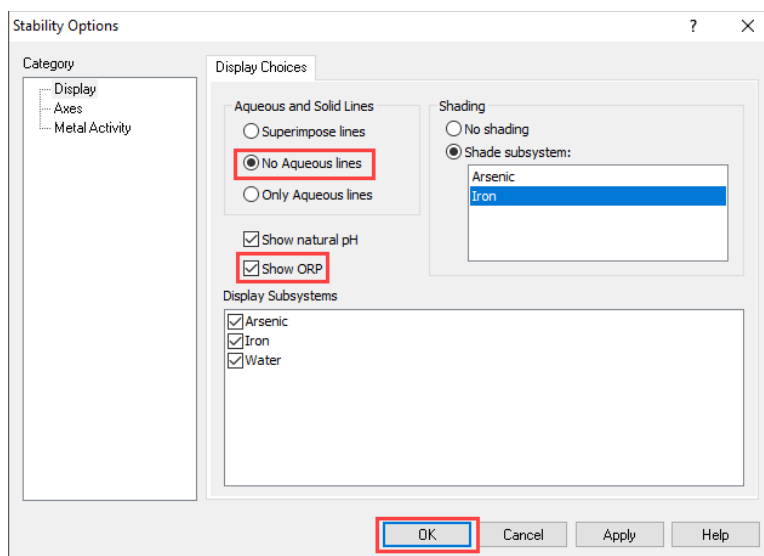
Note: Make sure that both **Fe** and **As** are enabled for Redox reactions. Use the arrow next to the **Re** button to expand the list.

You can also enable Redox reactions via the menu bar: **Chemistry > Model Options > Redox** tab. Make sure that Fe and As boxes are checked.

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



Click the **Specs** button and under the Display Choices tab check the following options:
 No aqueous lines
 Show ORP



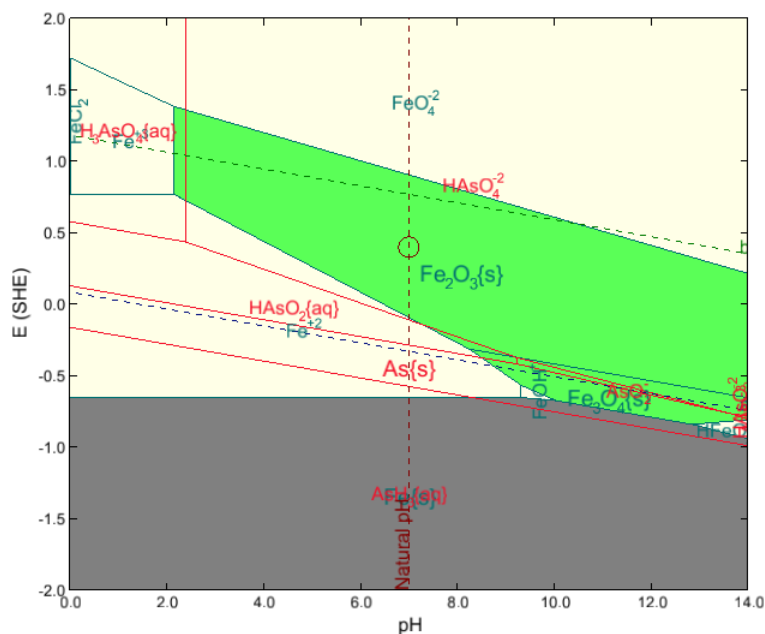
Click **OK** to close the Stability Options window

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-As-H₂O system at 25 °C and 1 atm.



The elemental arsenic field overlaps with the corrosion range of Fe in most of the pH range provided that the conditions are reducing (absence of oxygen). This promotes inhibition because of the coupling of: Oxidation of Fe to Fe⁺² and the reduction of arsenates to elemental As. This promotes the deposition of a protective layer of As. This can only work in reducing environments; otherwise, the protective layer of As will oxidize and dissolve.

Implications of Stability Diagrams on Cathodic Protection

Cathodic protection works by shifting the potential of the metal into its immunity range. Stability diagrams can help you to answer the following questions:

What is the potential range that ensures that the metal stays in the immunity range?

What is the effect of environmental variables on the immunity domain?

We will explore the Fe-H₂O system at different temperatures and pressures to answer these questions.

Example 49: Effect of Temperature and Pressure on the Pourbaix Diagram of Fe-H₂O System

Starting the Simulation

Iron at 30 °C and 1 atm

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	Cathodic Protection	Stream Amount	Calculated
Name Style	Display Formula	Temperature	30 °C
Unit Set	Metric, Batch, Moles	Pressure	1 atm
Framework	AQ	pH Range	0-14 (Default)
Calculation Type	Stability Diagram	H ₂ O	55.5082 moles
Contact Surface	Fe		

Add a new **Stream**

Click on the new Stream and press **<F2>** to change the name to *Cathodic Protection*

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

Under the *Cathodic Protection* Stream add a new Stability Diagram calculation. Go to the **Add Calculation** button and select **Stability Diagram** calculation or by selecting the **Chemical 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 at 30C and 1 atm*

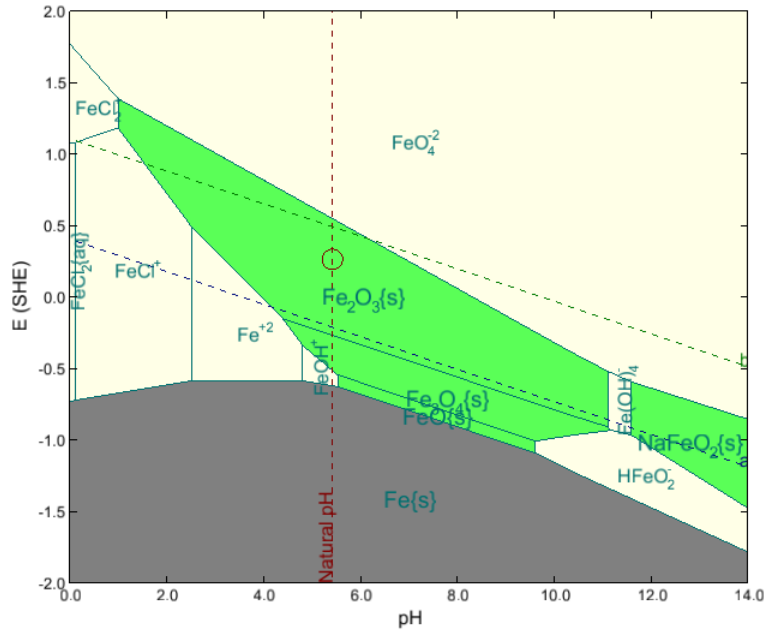
Under the **Contact Surface** grid type **Fe**

Iron at 300 °C and 100 atm

Go to the **Definition** tab, and change the Temperature and Pressure to 300°C and 100 atm
Click on the **Calculate** button or press the **<F9>** key

Analyzing the Results

Click on the **Chemical Diagram** tab ( **Stability Diagram**). This tab displays the Pourbaix Diagram for the Cu-H₂O-NH₃ system at 300 °C and 100 atm.



The immunity range in acidic and neutral solutions is weakly affected by temperature. However, the immunity range in alkaline solutions is shifted to much lower potentials which makes cathodic protection much more difficult.

Section 8. Introduction to Rates of Corrosion

In this section you are going to learn how to set up a Corrosion Rate calculation, how to study the effect of different variables on the corrosion rates of different alloys, such as temperature, pH, flow velocity, etc., and how to interpret the results when using this tool.

We will also explore how to interpret the results for the propensity to localized corrosion, polarization curves and heat treatment effects.

The screenshot displays the OLI Studio software interface for setting up a corrosion rate calculation. The main window is titled "Rates" and contains several sections:

- Stream Parameters:**

Variable	Value
Stream Amount (mol)	55.5082
Temperature (°C)	
Pressure (atm)	1.00000
- Calculation Parameters:**

Flow Type	Static
Effect of FeCO ₃ / FeS Scales	Include
- Inflows (mol):**

H ₂ O	55.5082
Fe	0.0
- Contact Surface:**

Carbon steel G10100 (generic)	
-------------------------------	--

On the right side, there are control options for the survey:

- Survey by: Temperature (dropdown), Specs...
- Then by (optional): None (dropdown), Specs...
- Vary: Independently, Together
- Calculate button (with a green checkmark icon)

A Summary panel on the right provides details about the calculation:

- 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
- Isothermal Calculation: 25.0000 °C 1.00000 atm, Calculation not done
- Temperature survey: Range 25.0 to 100.0 °C, Step size 5.0 °C, No. steps 15
- No secondary survey selected
- Polarization Curve Range: Range -2.0 to 2.0 V (SHE)

At the bottom of the Rates window, there are buttons for "Advanced", "Search", "Add as Stream", and "Export".

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. Note: As of version 11.5 and earlier, only the AQ thermodynamic framework supports the corrosion rate calculation.

Example 50: Corrosion rate of an oxygenated 0.1 m NaCl solution

Starting the Simulation

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

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

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

Add a new Stream

Click on the new Stream and press <F2> to change the name to *CR of carbon steel*

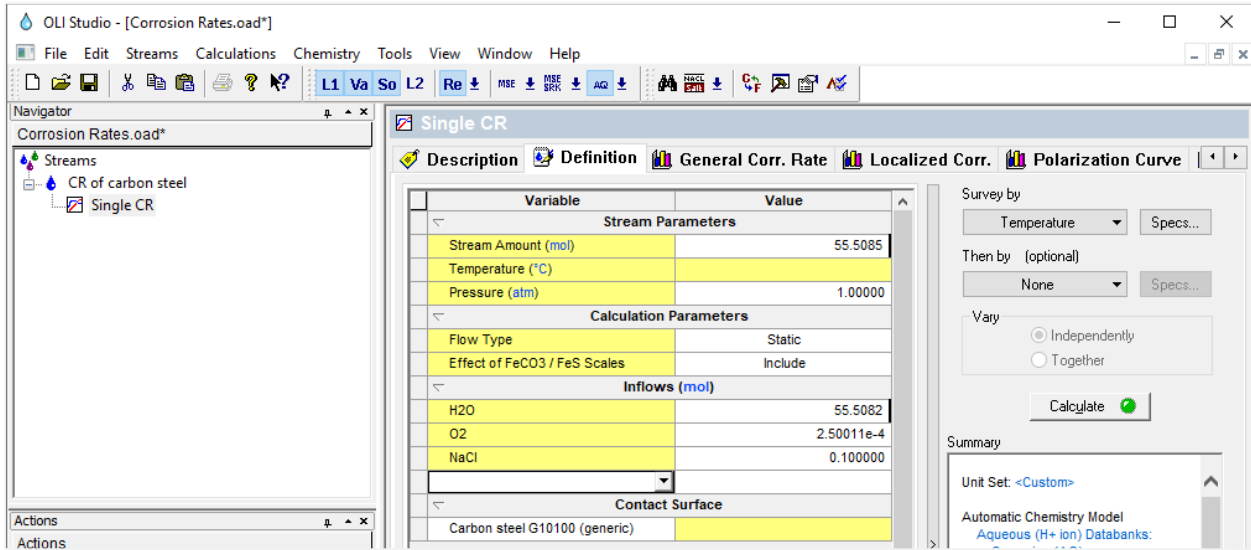
Select the **AQ** thermodynamic Framework

Click on the **Names Manager** Icon and select the **Formula** option

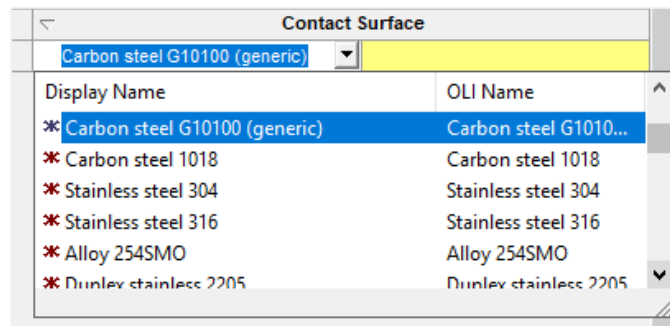
Click on the **Units Manager** Icon, and select Metric, Batch, Moles

Enter the composition, temperature and pressure of the stream given in the table above

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

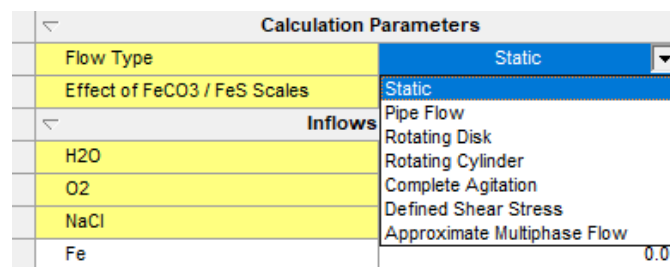


Note: By default, the software has selected **Carbon steel G10100 (generic)** as the default contact surface to perform the corrosion rates on. You can click on the white space of the **Carbon steel G10100 (generic)** name, and it will show a drop-down arrow. You can then click on the dropdown arrow,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



Additionally, the **Calculation Parameters** grid shows two options: (1) Flow Type and (2) Effect of FeCO₃ /FeS scales on corrosion rates.

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



Static

The solution is not flowing in this calculation.

Pipe Flow

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

Rotating disk

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

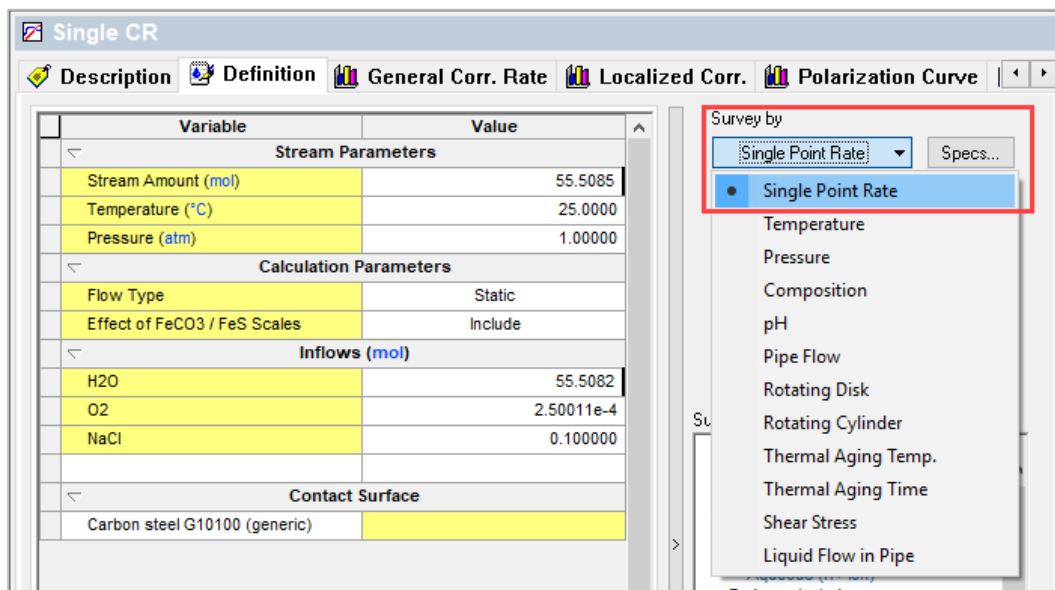
Rotating Cylinder

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

Complete Agitation

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

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



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

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

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

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

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

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


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

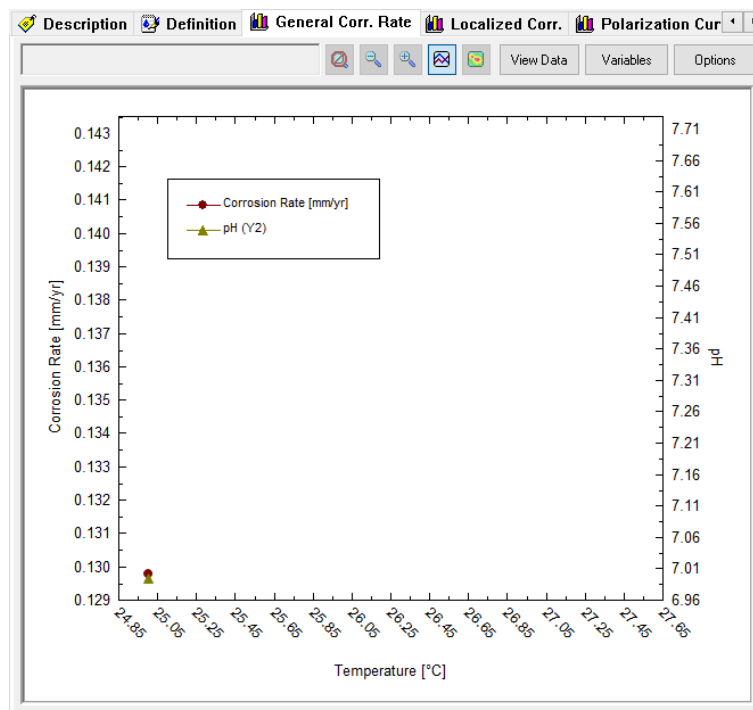
Flow Velocity Survey – In systems that are flowing, the flowrate of the stream can be varied.

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

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

Analyzing the Results

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



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

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

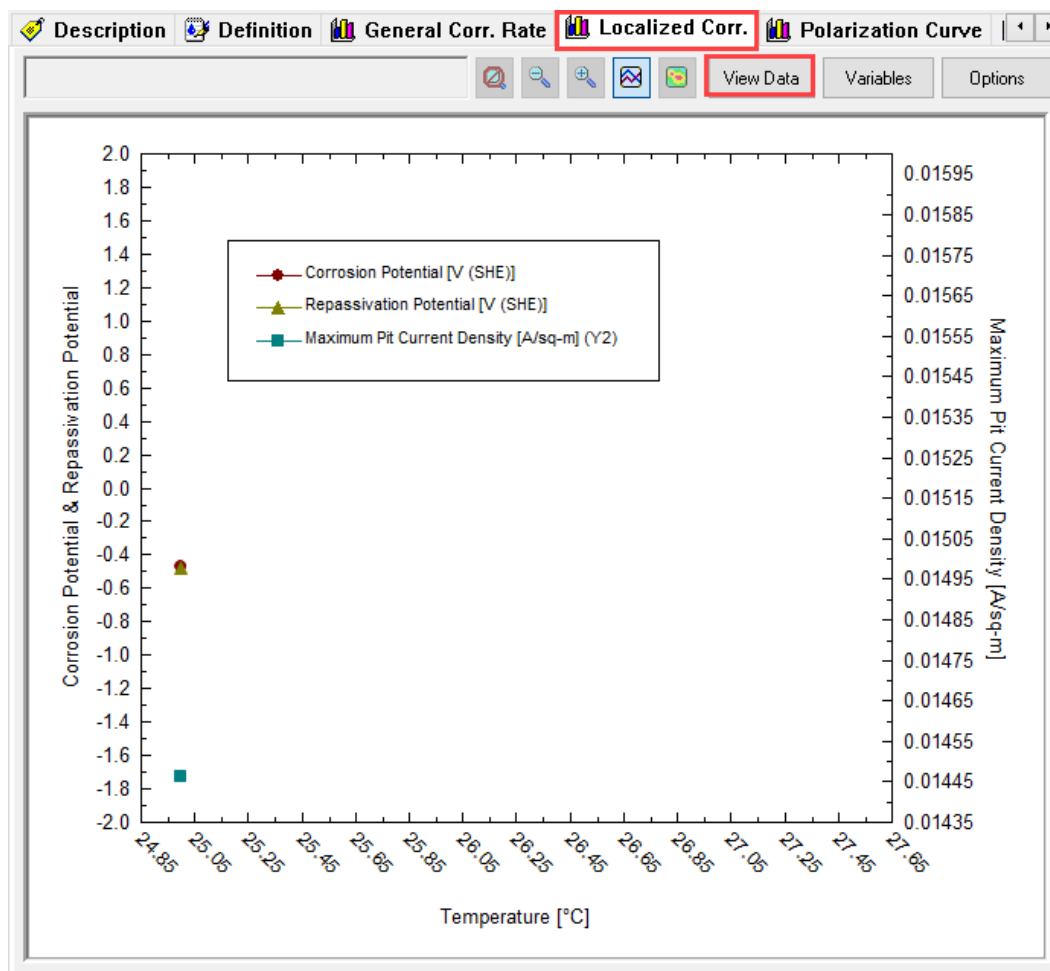
The predicted corrosion rate of carbon steel at 25 °C and 1 atm is ~0.13 mm/year when exposed to an oxygenated 0.1 m NaCl solution. It is important to highlight that this predicted corrosion rate is the corrosion rate once the system has reached a steady state.

Click on the **Localized Corr. Rate** tab (Localized Corr.). This tab displays a plot showing the results of three different calculated data:

Corrosion Potential (red dot)

Repassivation Potential (yellow triangle)

Maximum Pit Current Density (blue square)

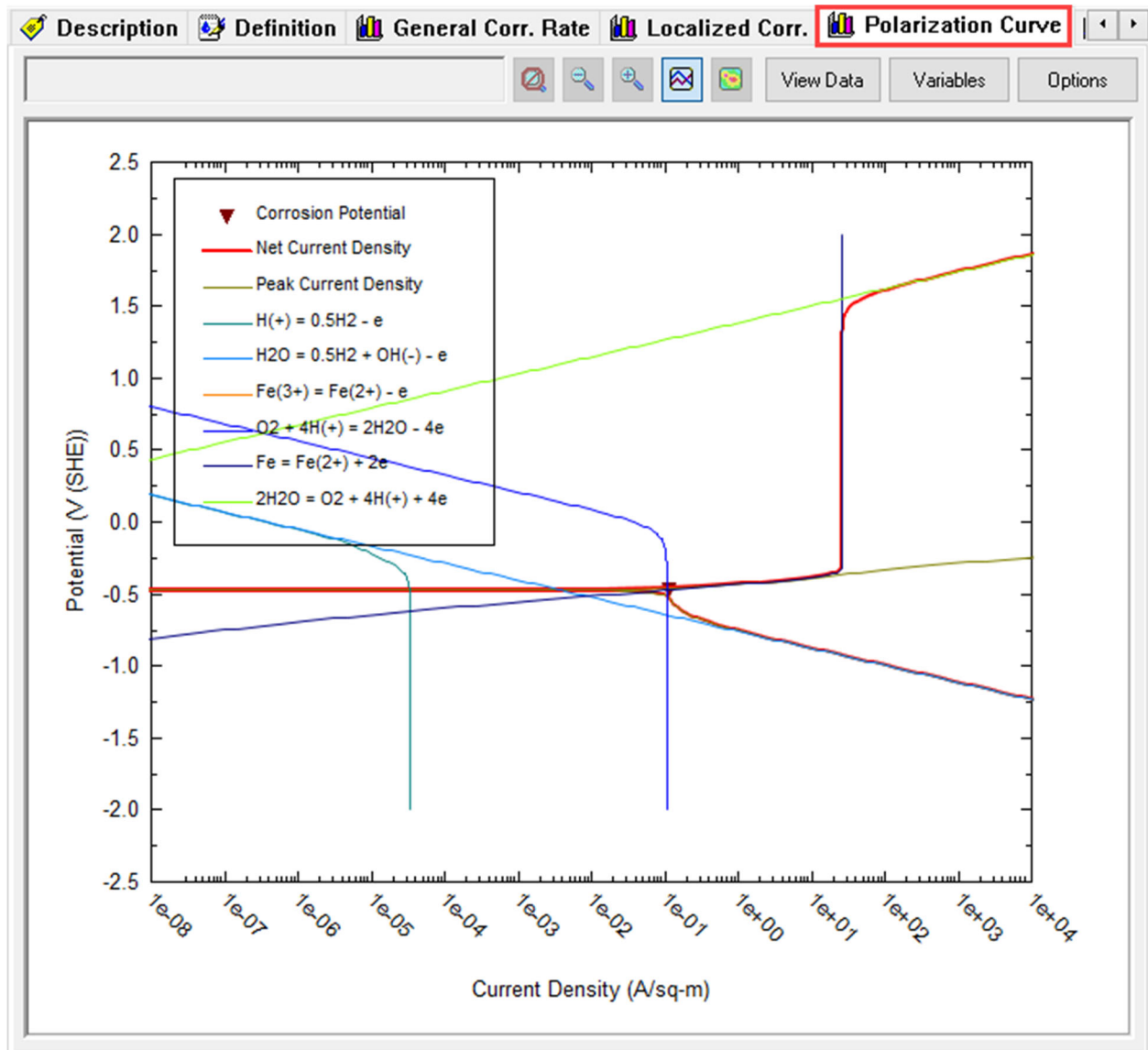


Click on the **View Data** button to see the results in tabulated form.

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

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

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



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

Exploring corrosion rate calculation options

Example 51: Corrosion in a Water-Filled Carbon Steel Tank

In the following example you are going to study the corrosion rate of a carbon steel tank with a volume of 10 m^3 tank (3.2 m high and 200 cm in diameter) that is filled to the top with water. The tank's wall thickness is 1.27 cm.

These are the operation conditions:

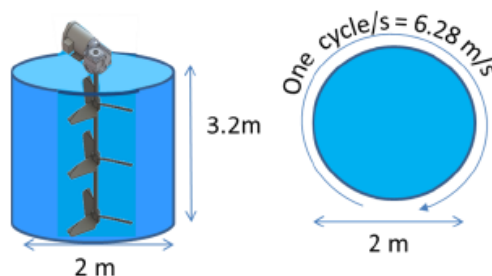
Sometimes the water in the tank remains static (mixer off), closed to the atmosphere

Some other times the tank is fully mixed (complete agitation)

The tank when operating has a variable speed mixer with a rotation speed between 0 and 12,000 rpm

At other times, the tank is open to the atmosphere. The effects of O_2 , CO_2 and flow will be studied.

We will evaluate each instance to compute the corrosion risk.



Starting the Simulation

First operation condition: Static flow, tank closed to the atmosphere at ambient conditions

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 of tank as a function of flow			
Calculation Settings		Stream Composition and Conditions	
Stream Name	CR vs flow	Stream Amount	10000 L
Calculation Type	Corrosion Rates	Temperature	25 °C
Name Style	Display Name	Pressure	1 atm
Unit Set	Metric, Batch, Concentration	Water	Calculated
Framework	AQ		
Contact surface	Carbon Steel G10100 (generic)		

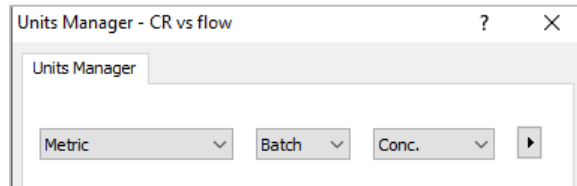
Add a new **Stream**

Click on the new Stream and press **<F2>** to change the name to *CR vs flow*

Select the **AQ** thermodynamic Framework

Click on the **Names Manager** Icon, and select the **Display Name** option, and click **OK**

Click on the **Units Manager** Icon, and select the **Metric, Batch, Conc.** option, and click **OK**



In the Definition tab, notice that the units of the Stream Amount changed from moles (mol) to liters (L).

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.

Change the **Rates** name to **Static Flow, 25C** using the **<F2>** key.

Leave the default Flow Type as **Static**

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.

Your screen should look like the image below.

Variable	Value
Stream Parameters	
Stream Amount (L)	10000.0
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Calculation Parameters	
Flow Type	Static
Effect of FeCO ₃ / FeS Scales	Include
Inflows (mg/L)	
H ₂ O	
Fe	0.0
Contact Surface	
Carbon steel G10100 (generic)	

Survey by: Single Point Rate

Then by (optional): None

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

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 output tab labeled **1** (next to the input tab), and check the results located in the **Corrosion Values** tab.

Variable	Value
Stream Parameters	
Stream Amount (L)	10000.0
Volume - Aqueous (L)	10000.0
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Corrosion Values	
Repassivation Potential (V (SHE))	99.9000
Corrosion Rate (mm/yr)	7.12696e-3
Corrosion Potential (V (SHE))	-0.552268
Corrosion Current Density (A/sq-)	6.14631e-3
Inflows (mg/L)	
H2O	9.96987e5
Contact Surface	
Carbon steel G10100 (generic)	

Input: **1**

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

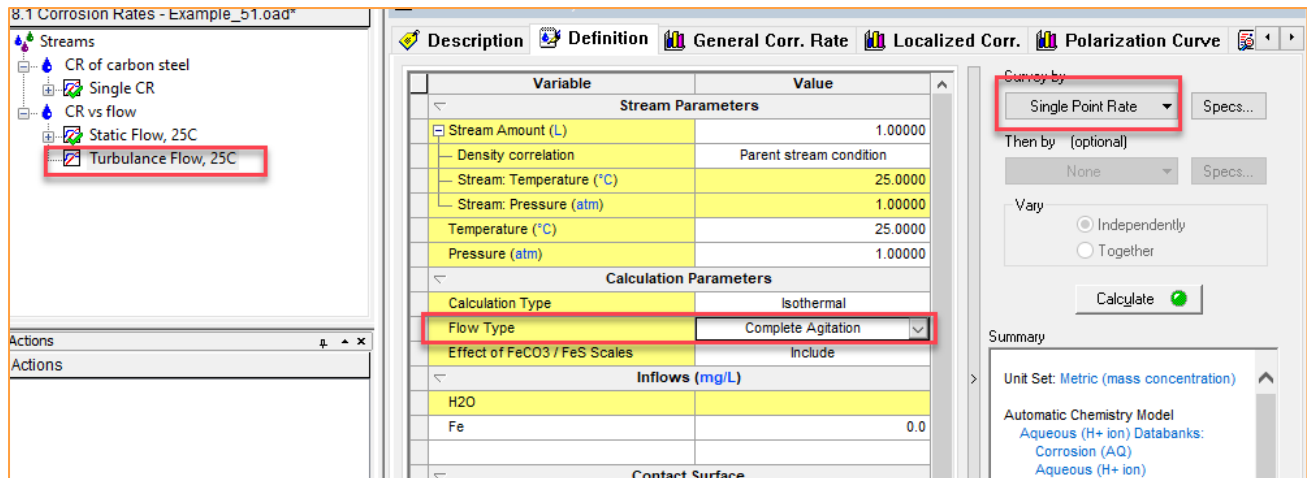
Summary
Unit Set: Metric (mass concentration)
Automatic Chemistry Model
Aqueous (H+ ion) Databanks:
Corrosion (AQ)
Aqueous (H+ ion)
Redox selected
Using K-fit Polynomials
T-span: 25.0 - 225.0
P-span: 1.0 - 1500.0
Isothermal Calculation
25.0000 °C 1.00000 atm
Calculation complete

The corrosion rate is 7.13×10^{-3} mm/yr. This is a negligible rate, since the thickness of the tank is ~ 12.7 mm, then corroding half the wall thickness would take about 900 years.

Second operation condition: Turbulent flow, tank closed to the atmosphere at ambient conditions

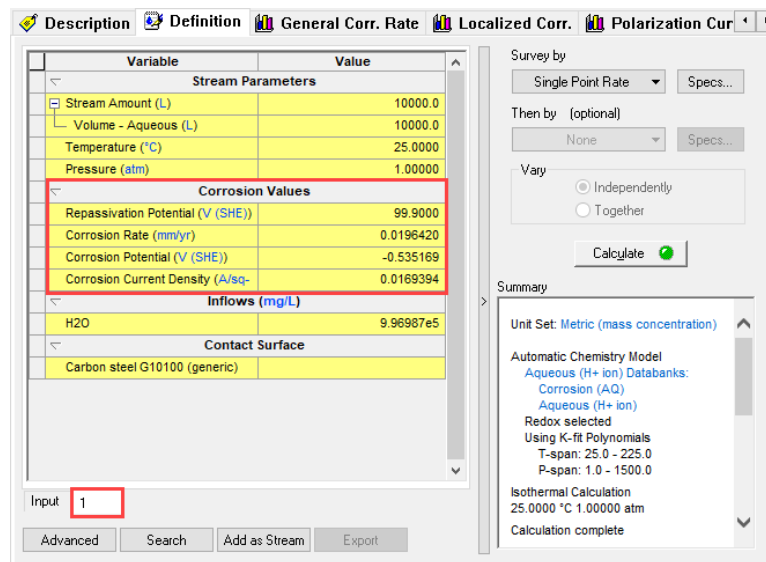
Under the stream 'CR vs Flow' add new corrosion rate calculation. Go to the **Add Calculation** button and select **Corrosion Rates** calculation or by selecting the **Add Corrosion Rates** icon in the Actions Pane. Change the **Rates** name to **Turbulent Flow, 25C** using the <F2> key. Change the default Flow Type to **Complete Agitation**. Leave the default alloy **Carbon steel G10100 (generic)** as the contact surface. Go to the **Survey by** option and select **Single Point Rate**.

Your screen should look like the image below.



Analyzing the Results

Click on the output tab labeled **1** (next to the input tab), and check the results located in the **Corrosion Values** tab.



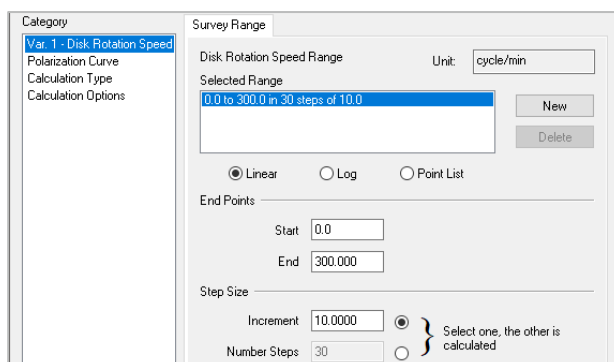
The corrosion rate increased 0.0196 mm/year, still a relatively low value.

Third operation condition: Varying flow, tank closed to the atmosphere at ambient conditions

Under the stream 'CR vs Flow' add new corrosion rate calculation. Go to the **Add Calculation** button and select **Corrosion Rates** calculation or by selecting the **Add Corrosion Rates** icon in the Actions Pane. Change the **Rates** name to **Varying Flow, 25C** using the <F2> key. Go to the **Survey by** button and select **Rotating Disk**. Under the **Calculation Parameters** grid, change the **Disk Diameter** to **200 cm**.

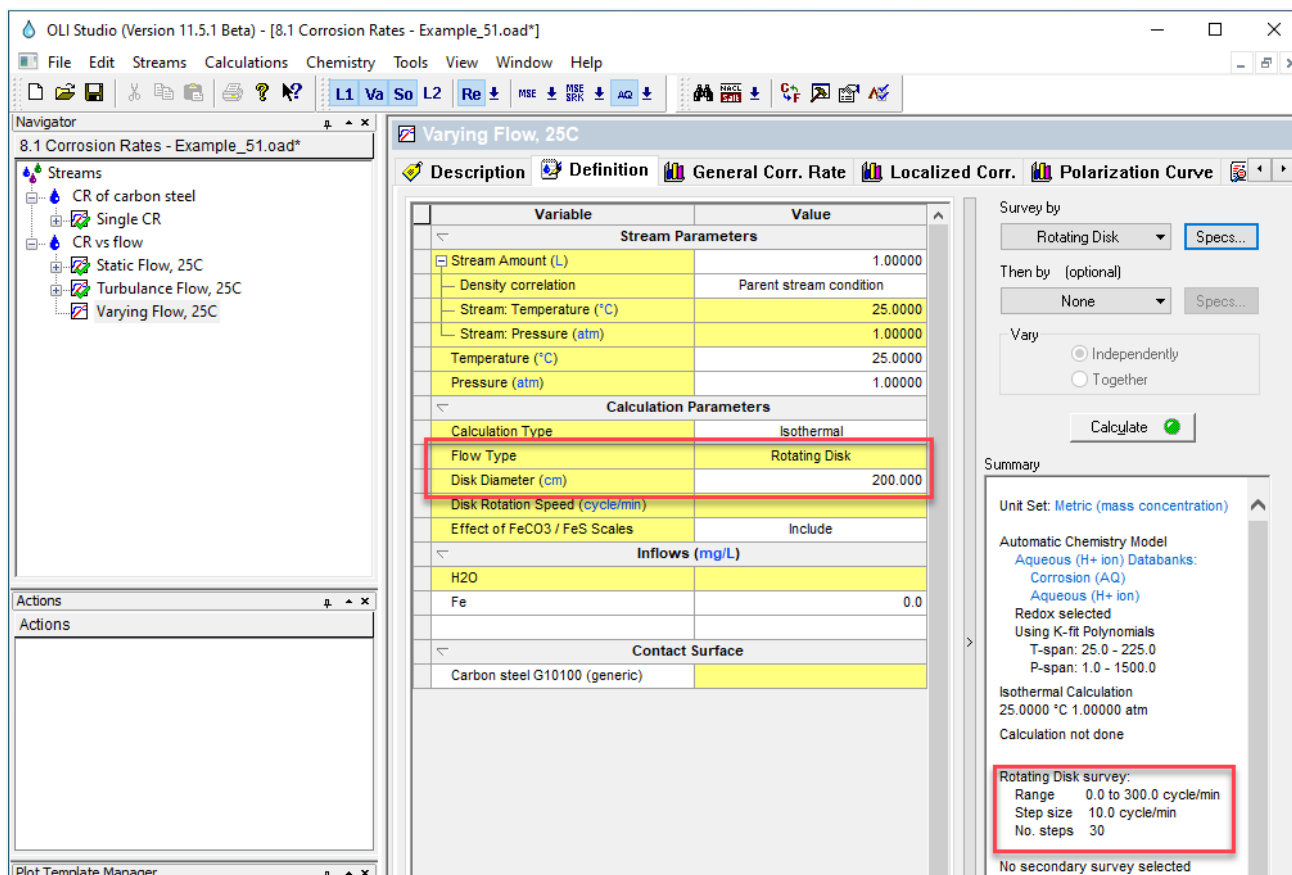
Note: At this point the vertical dimensions of the tank are unimportant. We will assume that the tank can be modeled like a rotating cylinder. The propeller rotates at 1200 rpm, although it is not expected that the wall velocity will approach this value, and so a lower value will be used (we still want it to be high enough to see the effects of shear).

The next step is to set the speed of the mixer. Go to the **Specs** button next to the **Rotating Disk** option. Change the Disk Rotation Speed Range from 0 to 300 cycles/min with an increment of 10 cycles/min. Then click **OK**.



Leave the default alloy **Carbon steel G10100 (generic)** as the contact surface


Your screen should look like the image below.

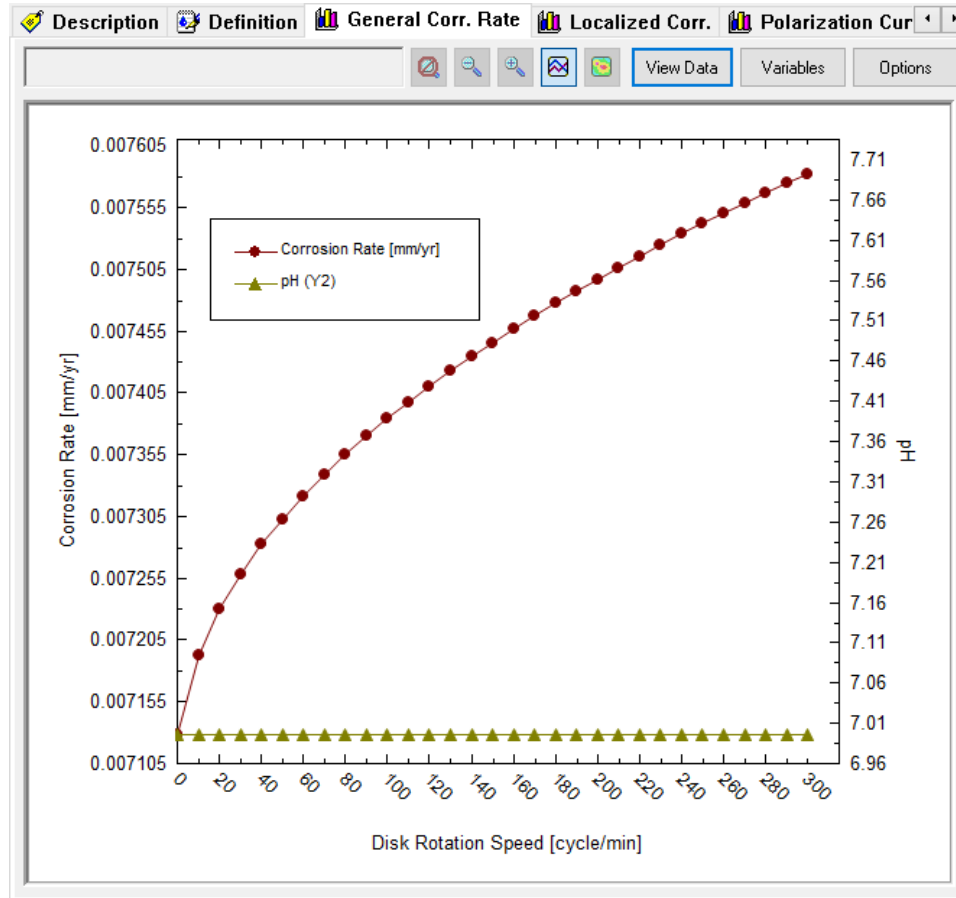


We are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key

It is time to **save** your file (**File >Save as...**) or using the **save** icon in the tool bar. You can save it under the same file created in the previous example named *Corrosion Rates*.

Analyzing the Results

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



The corrosion rate is computed to increase as the bulk liquid velocity increases from 0 to 300 rpm near the wall surface. The reason is straightforward; the higher velocity reduces the static water film thickness on the metal surface. This *diffusion layer* film limits the mass transfer of corrosion products and bulk chemicals to and from the surface. As the liquid velocity (and therefore shear force) increases, the film thickness decreases, and the concentration gradient increase. This increases the flux of materials to and from the surface, which increase corrosion rates.

Fourth operation condition: Static flow, tank open to the atmosphere (aerated with O₂ only) at ambient conditions

Open steel tanks are in contact with oxygen in the air. To simulate this, follow the steps below.

Under the stream 'CR vs Flow' add new corrosion rate calculation. Go to the **Add Calculation** button and select **Corrosion Rates** calculation or by selecting the **Add Corrosion Rates** icon in the Actions Pane Change the **Rates** name to **Static Flow, O₂** using the <F2> key

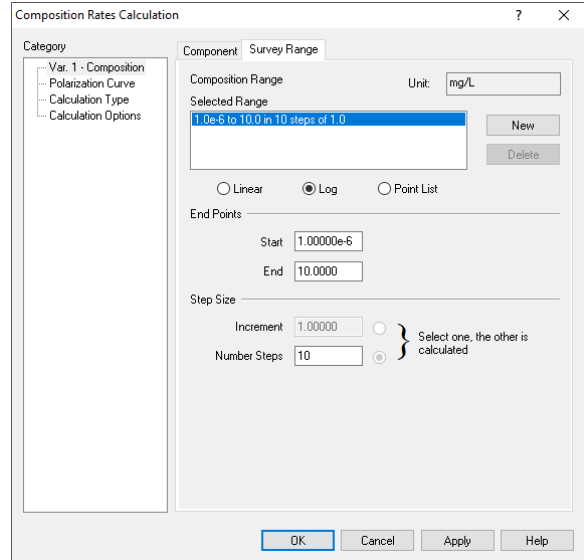
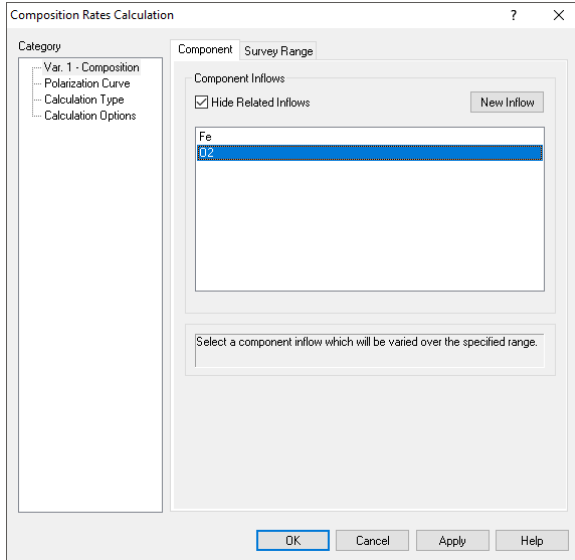
Add Oxygen (O₂) to the inflow grid

Leave the default Flow Type as **Static**

Go to the *Survey by* button and select **Composition**

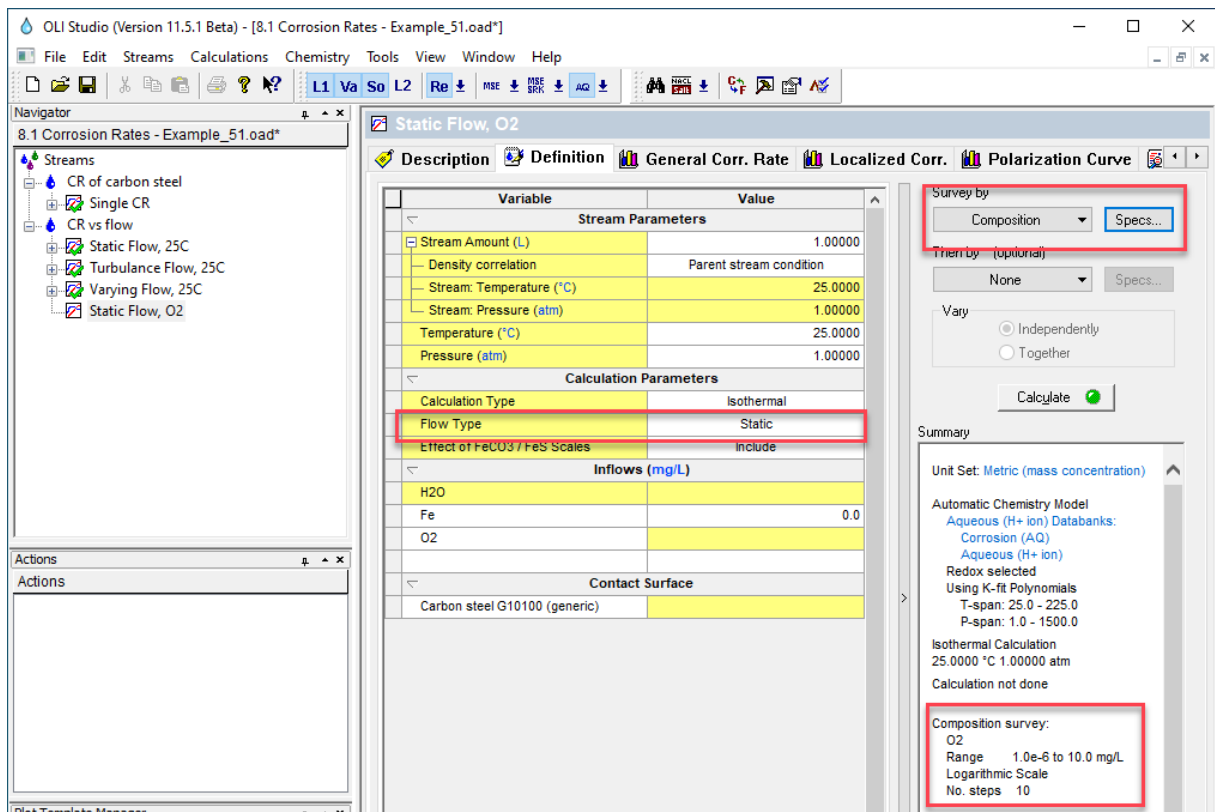
The next step is the concentration range of oxygen. Go to the **Specs** button next to the **Composition** option. This will open a new window.

Under **component** select (click on) O2. Then select the **Survey Range** tab and enter the Survey Range as follows: Log Scale, Start=1e-6, End=10, Steps=10. Then click **OK**.




Leave the default alloy **Carbon steel G10100 (generic)** as the contact surface

Your screen should look like the image below.

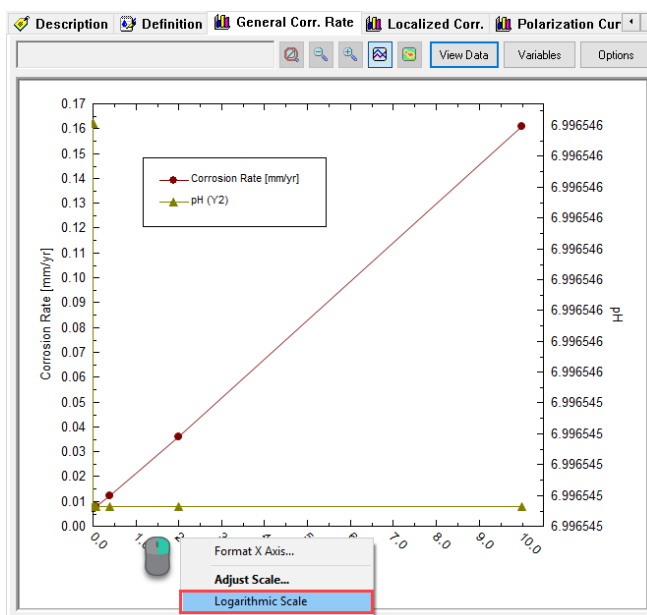


We are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key
It is time to **save** your file (**File >Save as...**) or using the **save** icon in the tool bar. You can save it under the same file created in the previous example named *Corrosion Rates*.

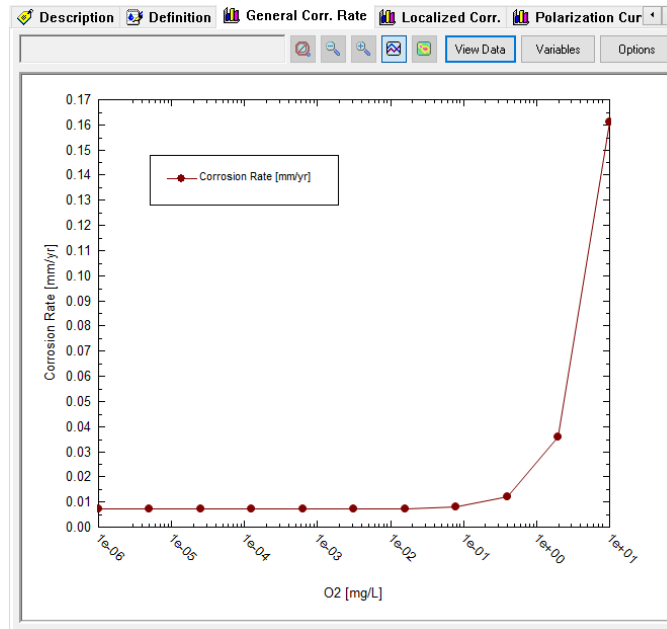
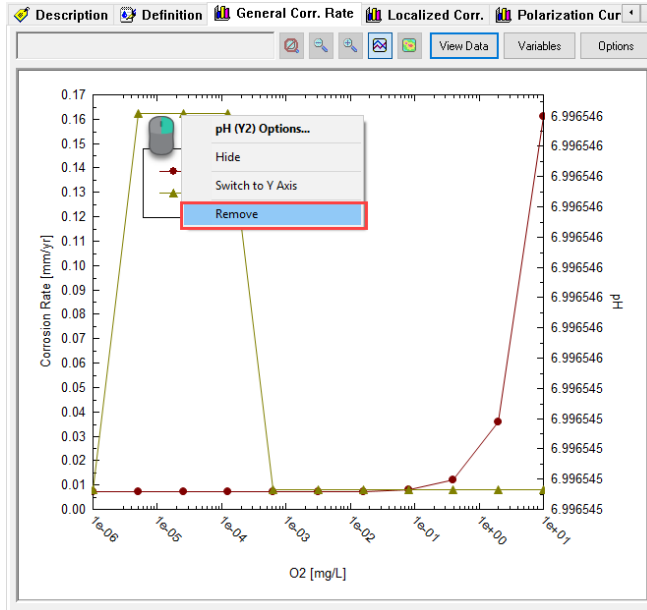
Analyzing the Results

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

Right-mouse click on the **X-axis** and change it to **Logarithmic Scale**



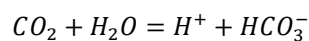
Right-mouse click on the **pH** curve and select **Remove**



The resulting plot shows the impact of oxygen on the corrosion rate. Corrosion increases by a factor of 20 once the concentration increases beyond 100 µg/l. Aerated water contains approximately 8 mg/l O₂. Corrosion on the tank wall is 0.16 mm/yr. At this rate, 50% of the 12.3 mm wall will be dissolved in 40 years.

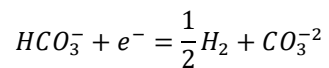
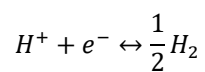
Fifth operation condition: Static flow, tank open to the atmosphere (aerated with O₂ and CO₂) at ambient conditions

The atmosphere contains ~400 ppmV CO₂. At this concentration 0.6 mg/l CO₂ is dissolved in water as molecular CO₂, this CO₂ hydrolyzes water to form the following reactants:



The resulting pH is about 5.6 at ambient conditions.

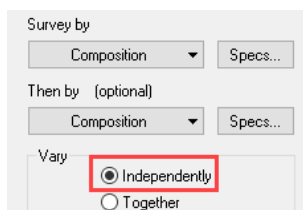
The impact of CO₂ on corrosion is two-fold, as two separate reactions occur at the metal surface:



To test the CO₂ impact, you will recalculate the corrosion rate using two CO₂ concentrations: 0 and 0.6 ppm.

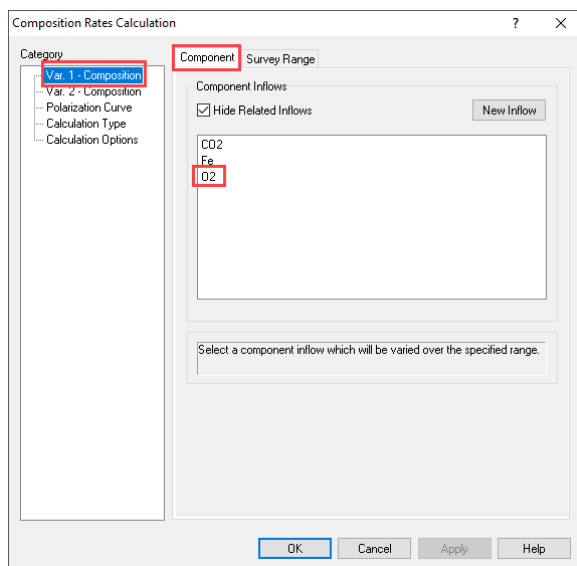
Under the stream '*CR vs Flow*' add new corrosion rate calculation. Go to the **Add Calculation** button and select **Corrosion Rates** calculation or by selecting the **Add Corrosion Rates** icon in the Actions Pane
Change the **Rates** name to **Static Flow, O2 and CO2** using the <F2> key
Add Oxygen (O₂) and carbon dioxide (CO₂) to the inflow grid
Leave the default Flow Type as **Static**

Go to the *Survey by* button and select Survey by **Composition** and then by **Composition** (as shown below)

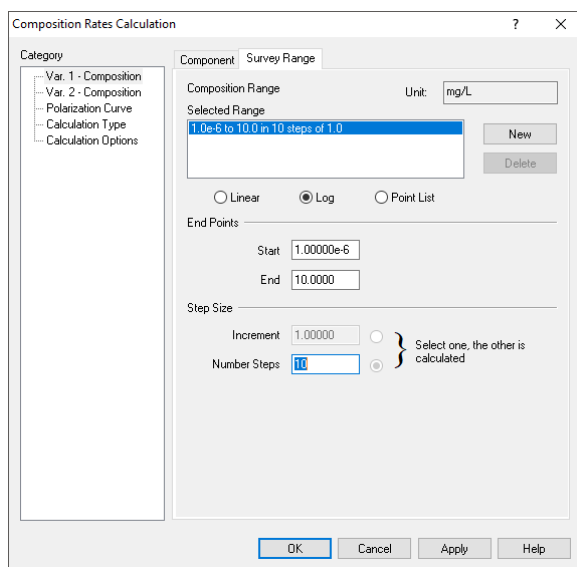


The next step is the concentration range of oxygen and carbon dioxide. Go to the **Specs** button next to the **Composition** option. This will open a new window.

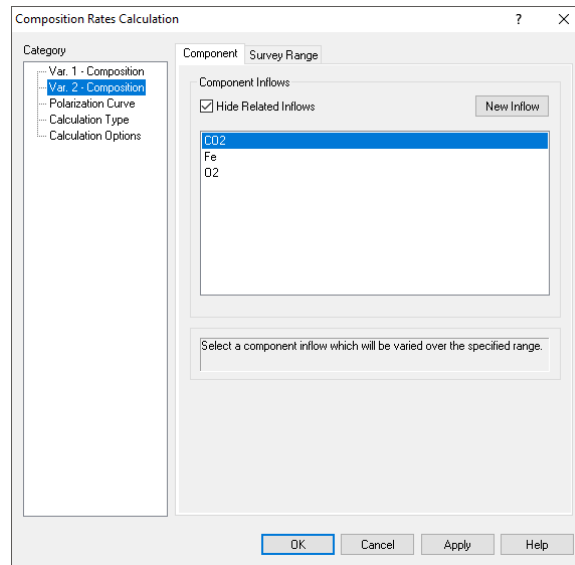
Under the **Category** section, make sure to select **Var. 1 -Composition**. Go to the **Component** tab, and select **O2**



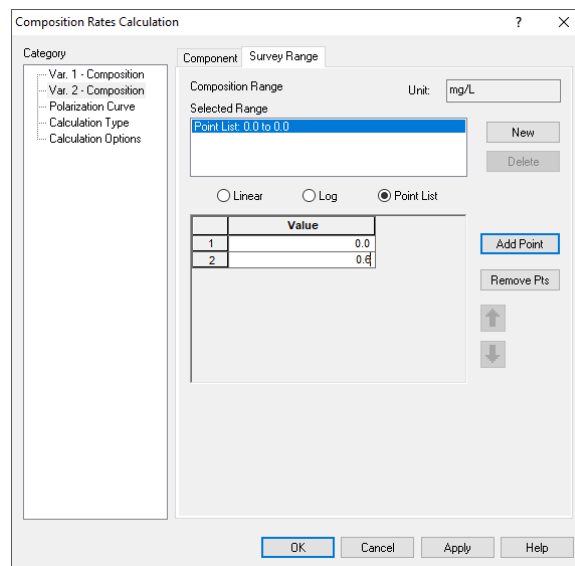
Then select the **Survey Range** tab and enter the Survey Range as follows: Log Scale, Start=1e-6, End=10, Steps=10. Then click **OK**.



Under the **Category** section, select **Var. 2 - Composition**. Go to the **Component** tab, and select CO2



Then select the **Survey Range** tab. Select the Point List option. Create two points with values of 0 and 0.6 mg/L. Then click **OK**.



Leave the default alloy **Carbon steel G10100 (generic)** as the contact surface

Your screen should look like the image below.

The screenshot shows the OLI Studio software interface for a simulation titled "Static Flow, O2 and CO2". The main window is divided into several sections:


- Navigator:** Shows a tree view of simulation components, including "Static Flow, O2 and CO2" which is currently selected.
- Main Panel:** Contains a table of parameters and a "Calculate" button.

Variable	Value
Stream Parameters	
Stream Amount (L)	1.00000
Density correlation	Parent stream condition
Stream: Temperature (°C)	25.0000
Stream: Pressure (atm)	1.00000
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Calculation Parameters	
Calculation Type	Isothermal
Flow Type	Static
Effect of FeCO ₃ / FeS Scales	Include
Inflows (mg/L)	
H ₂ O	
Fe	0.0
O ₂	
CO ₂	
Contact Surface	
Carbon steel G10100 (generic)	
- Summary Panel:** Provides details about the simulation setup, including the unit set (Metric), automatic chemistry model, and survey parameters for O₂ and CO₂.

We are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key

It is time to **save** your file (**File > Save as...**) or using the **save** icon in the tool bar. You can save it under the same file created in the previous example named *Corrosion Rates*.

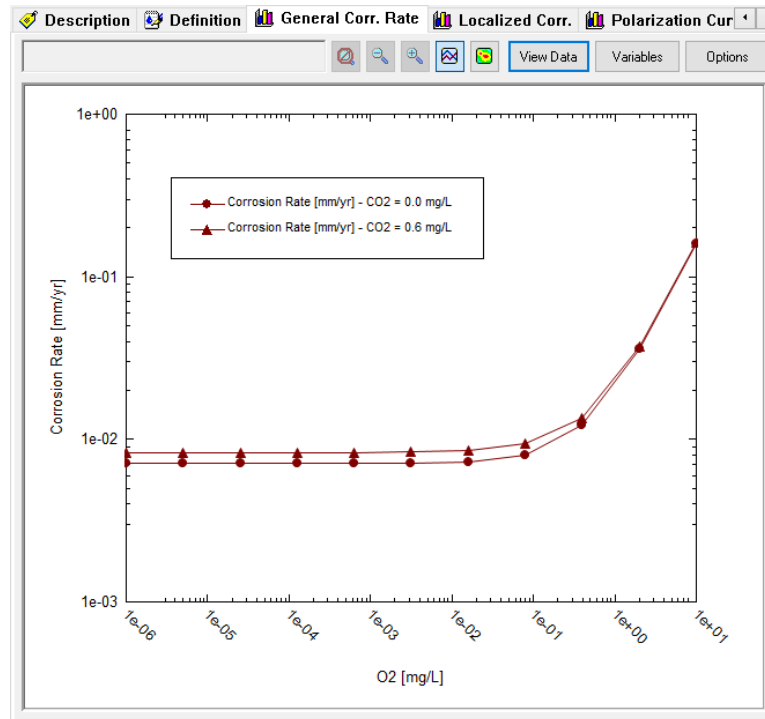
Analyzing the Results

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

Right-mouse click on the X-axis and change it to **Logarithmic Scale**

Right-mouse click on the Y-axis and change it to **Logarithmic Scale**

Right-mouse click on the pH curve and select **Remove Series**

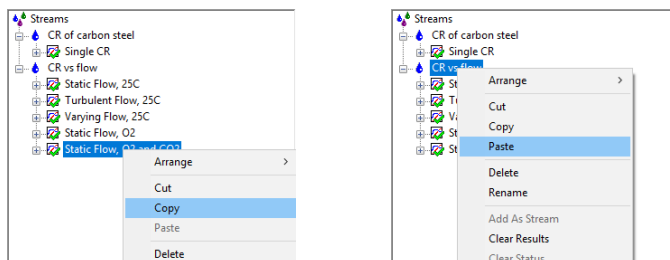


The effects of CO₂ are small, particularly in relation to the oxygen effects. The Corrosion rates at low O₂ content are about 0.0071 mm/yr with no CO₂ and 0.0083 mm/yr with 0.6 mg/l CO₂; a small difference between two small rates. At 10 mg/l O₂ the corrosion rate is 0.16 mm/y and it is the same with and without CO₂. Thus, CO₂ has no effect on corrosion at high O₂ concentrations meaning that the surface is corroded by oxygen and small concentrations of CO₂ does not change this rate.

Sixth operation condition: 300 cycles/min flow, tank open to the atmosphere (aerated with O₂ and CO₂) at ambient conditions

Lastly, you will look at the effects of shear rates on the tank in contact with CO₂ and O₂.

Copy (right-mouse click or Ctrl+C) 'Static Flow, O₂ and CO₂' corrosion calculation, and **paste** (right-mouse click or Ctrl+V) under the stream 'CR vs Flow'



- Change the **Static Flow, O₂ and CO₂-1** name to **300 rpm flow, O₂ and CO₂** using the <F2> key
- Add** Oxygen (O₂) and carbon dioxide (CO₂) to the inflow grid
- Change the Flow Type from **Static** to **Rotating Cylinder**
- Set** the **Rotor Diameter** to 200 cm
- Set** the **Rotor Rotation** to 300 cycles/min
- Leave the default alloy **Carbon steel G10100 (generic)** as the contact surface

Your screen should look like the image below.

300 rpm flow, O₂ and CO₂

Variable	Value
Stream Parameters	
Stream Amount (L)	1.00000
Density correlation	Parent stream condition
Stream: Temperature (°C)	25.00000
Stream: Pressure (atm)	1.00000
Temperature (°C)	25.00000
Pressure (atm)	1.00000
Calculation Parameters	
Calculation Type	Isothermal
Flow Type	Rotating Cylinder
Rotor Diameter (cm)	200.000
Rotor Rotation (cycle/min)	300.000
Effect of FeCO ₃ / FeS Scales	Include
Inflows (mg/L)	
H ₂ O	
O ₂	
CO ₂	
Contact Surface	
Carbon steel G10100 (generic)	

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:
 O₂
 Range 1.0e-6 to 10.0 mg/L
 Logarithmic Scale
 No. steps 10

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

Analyzing the Results

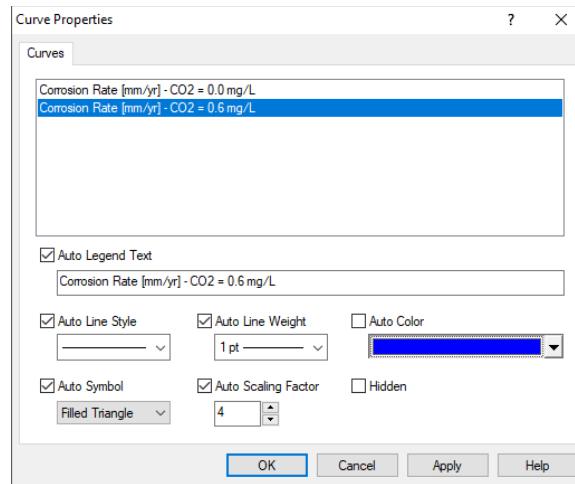
Click on the **General Corr. Rate** tab ( General Corr. Rate). This tab displays a plot showing the results of corrosion rate and pH.

Right-mouse click on the **X-axis** and change it to **Logarithmic Scale**

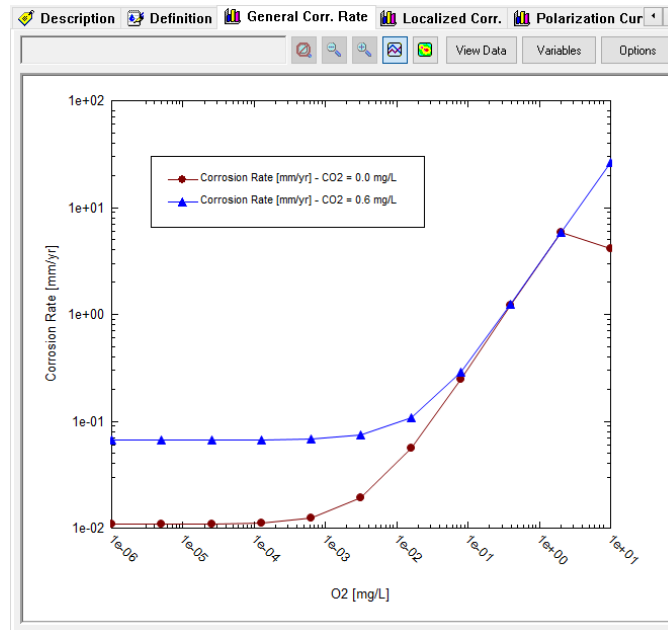
Right-mouse click on the **Y-axis** and change it to **Logarithmic Scale**

Right-mouse click on the **pH** curve and select **Remove Series**

Double click on the CO₂=0.6 mg/L. This will open a new window. Change the color to **blue**.



The plot should look like the image below.



The 0.6 mg/L CO₂ curve shifted to higher values at low O₂ concentrations compared to no CO₂ presence. Now, when comparing the corrosion rate for the 0.6 mg/L CO₂ concentration at 300 rpm vs static conditions, the rates are 0.067 mm/year and 0.008 mm/year respectively. The effect of shear at high O₂ concentrations (right side of the plot) is also pronounced. Corrosion is still dominated by O₂ attack, but the rate is now over 10 mm/year, about 100x greater than the static conditions.

Gas condensate corrosion

Example 52: Condensed overhead gas and mitigation strategies

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

Diethanolamine is used to neutralize an acid gas containing carbon dioxide (CO₂) and hydrogen sulfide (H₂S). The diethanolamine is regenerated and the acid gases are driven off in a stripper. The off gas from this stripper is saturated with water vapor. As these gases cool, they will condense. This condensate can be very corrosive. The plant's service life can be shortened considerably due to these condensed acid gases.

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

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

Starting the Simulation

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

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

Add a new **Stream**

Click on the new Stream and press **<F2>** to change the name to *Gas Condensate*

Select the **AQ** thermodynamic Framework

Click on the **Names Manager** Icon and select the **Formula** option

Click on the **Units Manager** Icon, and select Metric, Batch, Mole Fraction

Enter the composition, temperature and pressure of the stream given in the table above

Go to the **Add Calculation** button and select **Corrosion Rates** calculation or by selecting the **Add Corrosion Rates** icon in the Actions Pane.

Go to the **Survey by** option and select **Single Point Rate**. Change the name to **Gas Cond. Dew Point**.

Change the Flow Type from Static to **Pipe Flow**.

Specify the **Pipe Diameter** = 10 cm and the **Pipe Flow Velocity** = 2 m/s.

Leave the default alloy **Carbon steel G10100 (generic)** as the contact surface

Your screen should look like the image below.

The screenshot shows the OLI Studio interface for a calculation named "Gas Cond. Dew Point". The main window is divided into several panes:

- Navigator:** Shows a tree view of the simulation setup, including streams like "CR of carbon steel", "Single CR", "CR vs flow", "Static Flow, 25C", "Turbulence Flow, 25C", "Varying Flow, 25C", "Static Flow, O2", "Static Flow, O2 and CO2", "300 rpm flow, O2 and CO2", "Gas condensate", and "Gas Cond. Dew Pont."
- Actions:** A pane for managing actions.
- Plot Template Manager:** A pane for managing plot templates.
- Main Calculation Window:** Displays a table of parameters and a summary.

Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5082
Temperature (°C)	38.0000
Pressure (atm)	1.20000
Calculation Parameters	
Calculation Type	Isothermal
Flow Type	Pipe Flow
Pipe Diameter (cm)	10.0000
Pipe Flow Velocity (m/s)	2.00000
Effect of FeCO ₃ / FeS Scales	Include
Inflows (mole %)	
H ₂ O	5.42000
CO ₂	77.4000
N ₂	0.0200000
H ₂ S	16.6000
CH ₄	0.500000
C ₂ H ₆	0.0300000
C ₃ H ₈	0.0300000
Fe	0.0
Contact Surface	
Carbon steel G10100 (generic)	

Summary:

- Unit Set: Metric (mole fraction)
- 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: 38.0000 °C 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
- Metal: Iron/Mild steel, Carbon steel G10100 (generic)
- Flow Type: Pipe Flow, Diameter 10.0000 cm, Velocity 2.00000 m/s, Scales included - passivating films included.

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

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

Under the **Category** section, select **Calculation Type**

Change the Type of Calculation from Isothermal to **Dew Point**. Make sure that radio button for temperature is selected since we are going to calculate the Dew Point temperature for this example. Then click **OK**. Notice that the input grid has been updated:

Calculation Parameters	
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 ₃ / FeS Scales	Include

You could have also used the drop-down arrow next to the “Calculation Type” box to directly pick a dew point (or any other required) calculation type.

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

It is time to **save** your file (**File > Save as...**) or using the **save** icon in the tool bar. You can save it under the same file created in the previous example named *Corrosion Rates*.


Analyzing the Results

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

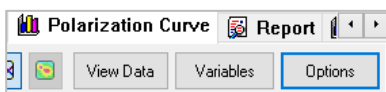
Click on the **View Data** button to see the results in tabulated form.

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

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

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

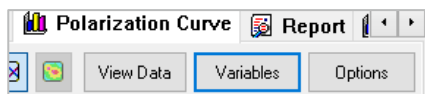
Click on the **Options** button. This will open a new window.



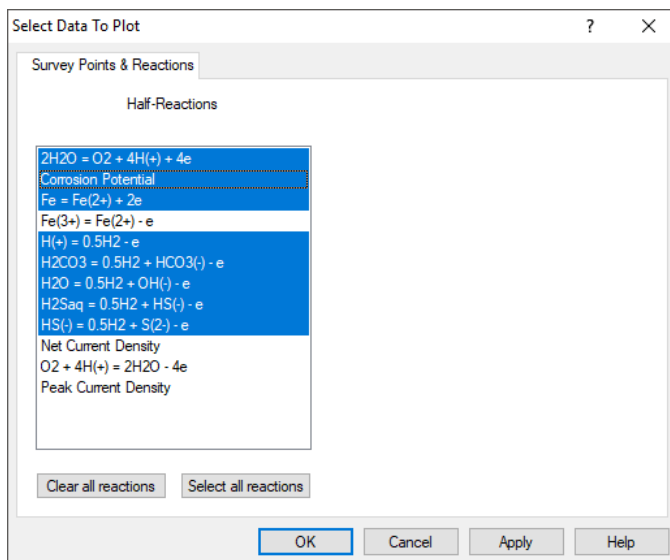
Under the **Category** section select **X axis**. Change the **Minimum** to 1e-6 and **Maximum** to 1e6.

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

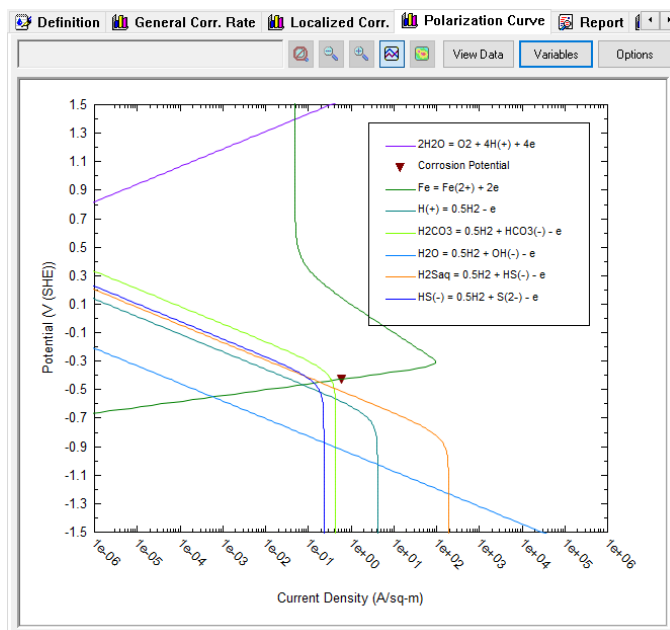
Click on the **Variables** button. This will open a new window.



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



Your polarization curve should look like the image below.



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

This is a measured potential vs. current density plot. The anodic portion (**green curve**) is the carbon steel. There are cathodic reactions. The sum of the cathodic currents adds up to the anode curve at a single point: The corrosion potential (represented by the inverted red triangle ▼) with a value of -0.43 V vs SHE. At the corrosion

potential, the anodic and cathodic currents are equal, and this value is also known as the i_{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 H_2CO_3 (light green line). The next contributors are H_2S (orange line) and HS^- (blue line) equally. After that is H^+ (turquoise line). Water reduction (light blue line), contributes the least to corrosion.

Mitigation Strategies

There are several mitigating solutions to this corrosion problem.

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

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

Changing alloys could mitigate the corrosion problems as well.

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

Adjusting the solution chemistry

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

Single Point– Set pH Calculation

Click on the 'Gas Condensate' stream and **go** to the **Add Calculation** button and select **Single Point** calculation or by selecting the **Add Single Point** icon in the Actions Pane.

Change the name to **DEA** using the <F2> key.

Add DEA in the inflows grid. (It should have changed to the formula name: $\text{HN}(\text{C}_2\text{H}_4\text{OH})_2$)

Go to the **Type of Calculation** option and select **Set pH**

Change the **Target pH** to 7.5

Click on the drop-down arrow for the pH Base Titrant and select DEA (or $\text{HN}(\text{C}_2\text{H}_4\text{OH})_2$)

We have set up the calculation to adjust the amount of DEA to match the target value of $\text{pH}=7.5$.

Your screen should look like the image below.

OLI Studio - [Corrosion Rates.oad*]

File Edit Streams Calculations Chemistry Tools View Window Help

Navigator

Document1

Corrosion Rates.oad*

Streams

- CR of carbon steel
- CR vs flow
- Gas Condensate
- Gas Cond. Dew Point
- DEA

Actions

Plot Template Manager

Save

DEA

Description Definition Report File Viewer

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

Input

Advanced Search Add as Stream Export

Type of calculation

Set pH Specs...

Calculate

Summary

Unit Set: Metric (mole fraction)

Automatic Chemistry Model

Aqueous (H+ ion) Databanks:

Aqueous (H+ ion)

Using K-fit Polynomials

T-span: 25.0 - 225.0

P-span: 1.0 - 1500.0

Set pH Calculation

38.0000 °C

1.20000 atm

Target pH 7.50000

Acid Titrant:

Base Titrant: HN(C2H4OH)2

Calculation not done

For Help, press F1

NUM

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

It is time to **save** your file (**File >Save as...**) or using the **save** icon in the tool bar. You can save it under the same file created in the previous example named *Corrosion Rates*.

Analyzing the Results

Check the summary box to analyze the results.

Summary

Unit Set: Metric (mole fraction)

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

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

Phase Amounts
 Aqueous 31.6062 mol
 Vapor 99968.5 mol
 Solid 0.0 mol

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

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

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

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

Total and Phase Flows (Amounts)

column Filter Applied: Only Non Zero Values

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

Species Output (True Species)

Row Filter Applied: Only Non Zero Values

column Filter Applied: Only Non Zero Values

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

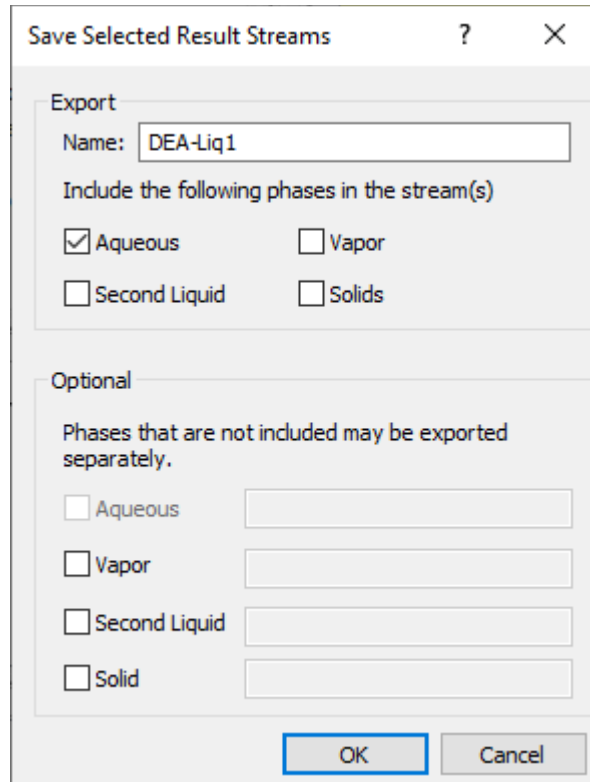
Recalculating the corrosion rate with DEA

We first need to capture the condensate from the DEA pH calculation. We want only the liquid portion to perform our corrosion rate calculation. This would represent the first drop of condensate from the gas stream.

The screenshot shows the OLI Studio interface for a DEA calculation. The main window displays a table of variables and values, categorized into Stream Parameters, Calculation Parameters, and Inflows (mole %). The 'Add as Stream' button is highlighted with a red box. The right-hand panel shows the 'Summary' section, which includes the 'Type of calculation' (Set pH), 'Unit Set' (Metric (mole fraction)), and 'Automatic Chemistry Model' (Aqueous (H+ ion) Databanks: Aqueous (H+ ion) Using K-fit Polynomials). The 'Summary' section also displays 'Set pH Calculation' parameters (38.0000 °C, 1.20000 atm, Target pH 7.50000, Acid Titrant: HCl, Base Titrant: HN(C2H4OH)2) and 'Phase Amounts' (Aqueous: 31.6197 mol, Vapor: 99968.5 mol, Solid: 0.0 mol). The 'Aqueous Phase Properties' section shows pH 7.50001, Ionic Strength 0.0160371 mol/mol, and Density 1.02648 g/ml. The 'Calc. elapsed time' is 0.111 sec, and the status is 'Calculation complete'.

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

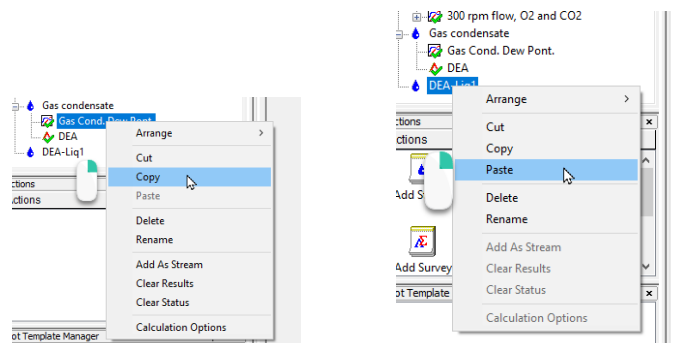
Click the **Add as Stream** button



Uncheck the following boxes: **Second Liquid, Vapor, and Solids**. This removes these phases from the saved stream. Click the **OK** button

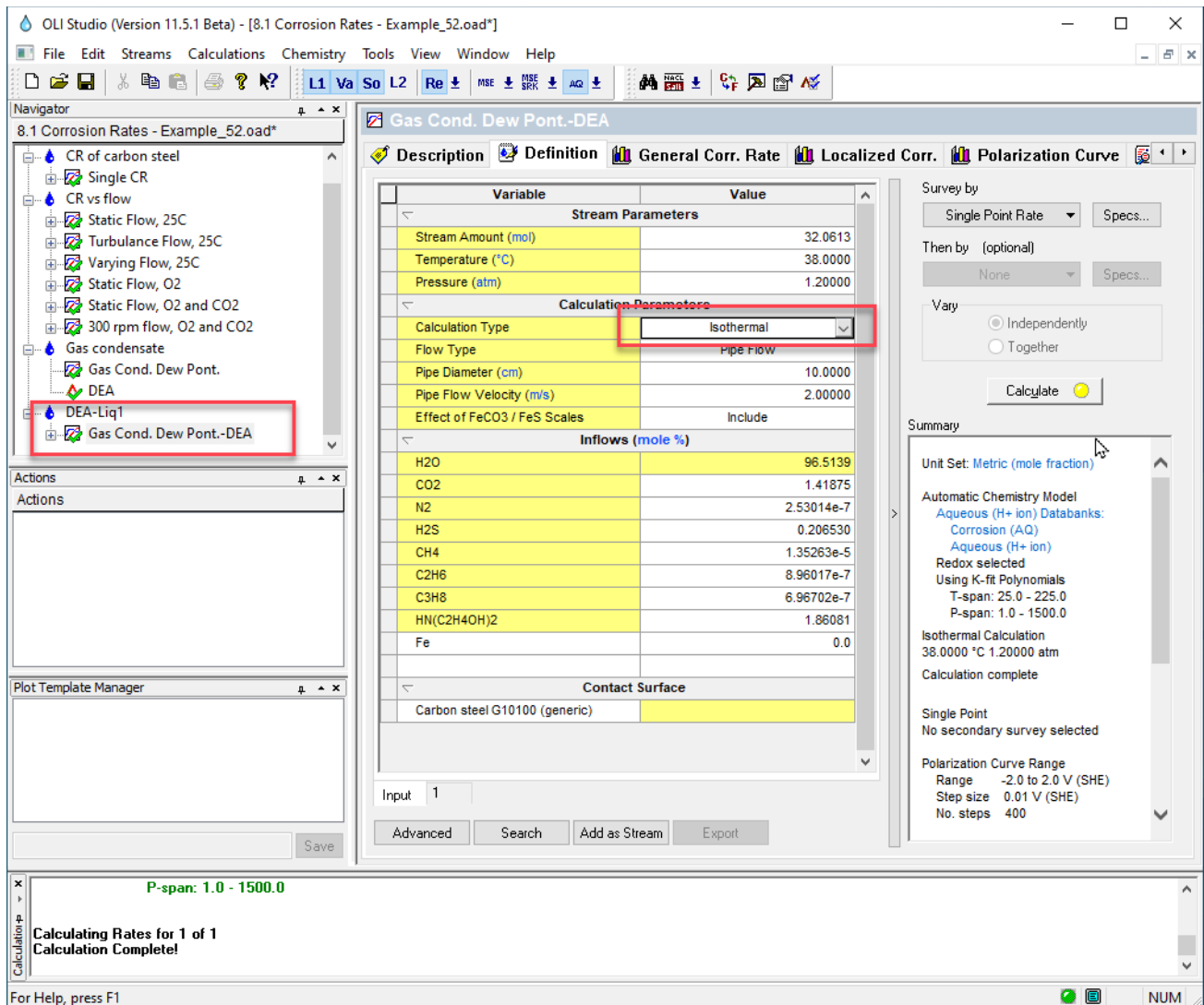
We now can recalculate the corrosion rate with DEA in the stream. This represents some DEA entrained in the vapor phase as the gas leaves the regenerator.

- **Copy** 'Gas Cond. Dew Point' corrosion calculation from the **Gas condensate** stream, and **paste** it under the stream '**DEA-Liq1**'



Change the name to **Gas Cond. Dew Point DEA** using the **<F2>** key
 The added DEA is already in the inflows grid.
 Leave the default alloy **Carbon steel G10100 (generic)** as the contact surface
 Change the calculation type to **Isothermal**

Your screen should look like the image below.



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

It is time to **save** your file (**File > Save as...**) or using the **save** icon in the tool bar. You can save it under the same file created in the previous example named *Corrosion Rates*.

Analyzing the Results

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

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

	Temperature	Corrosion Rate	pH
	°C	mm/yr	
1	38.0000	0.480601	7.50001

Notice that the corrosion rate has decreased from 0.7 mm/year to 0.48 mm year. The pH is 7.6, and it remained like the target value of 7.5. Based on these results neutralizing the pH had a partial effect on corrosion reduction.

Changing the Alloy

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

13%Cr Stainless Steel

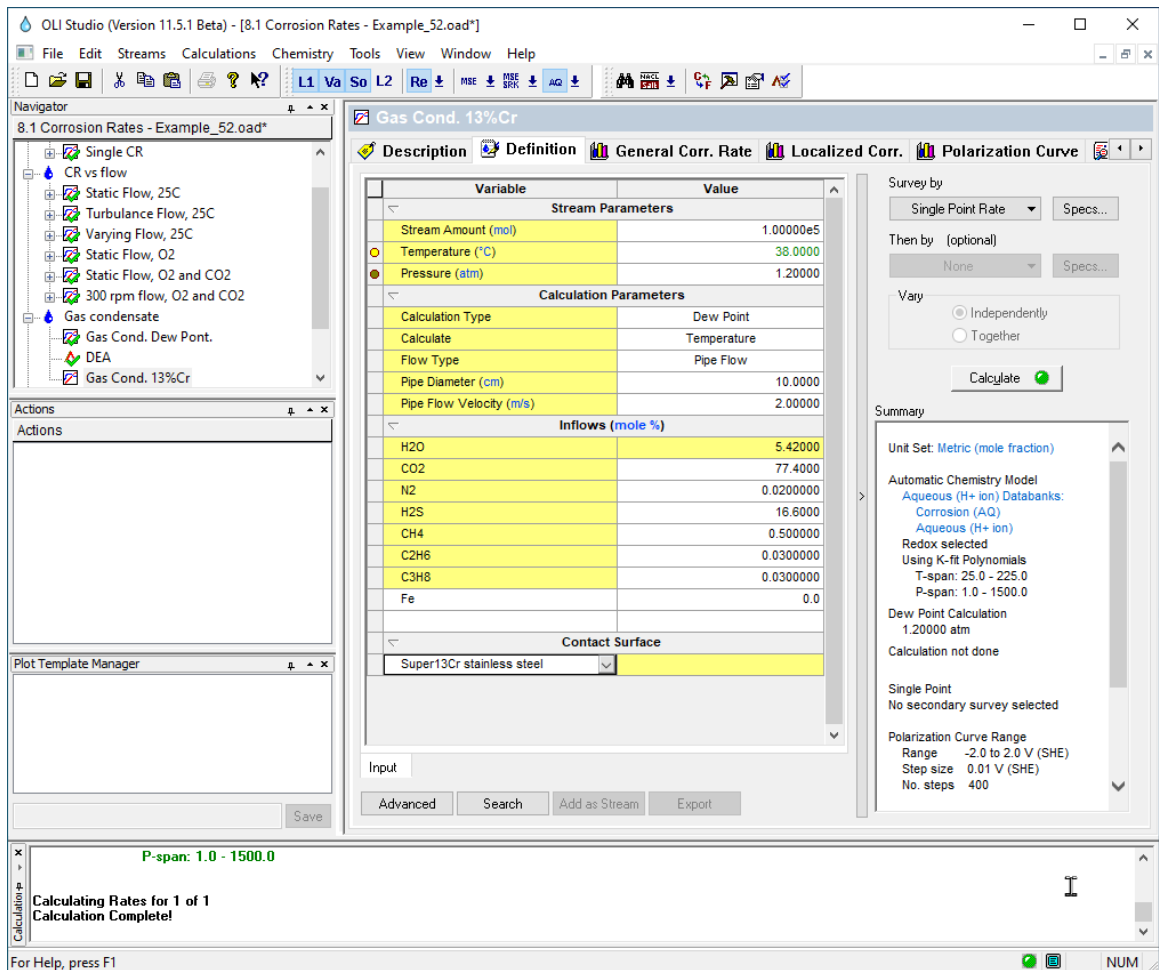
Copy 'Gas Cond. Dew Point' corrosion calculation, and **paste** it under the stream 'Gas Condensate'

Change the name to **Gas Cond. 13%Cr** using the <F2> key.

Notice that in the inflows, copying and pasting does not bring the DEA and its composition to this corrosion calculation. The reason why is because the DEA was added at the corrosion rate calculation level, and not at the stream level.

Change the contact surface to Super13%Cr stainless steel

Your screen should look like the image below.



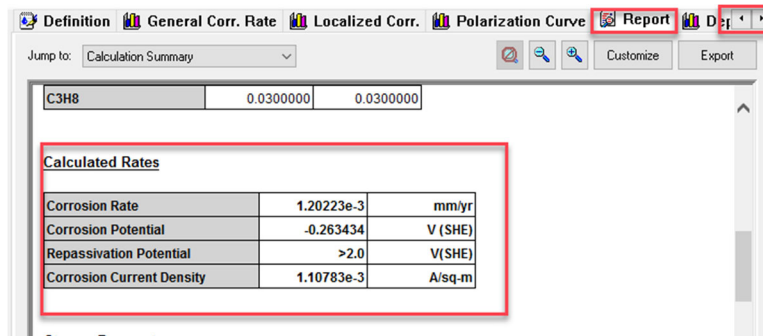
Now, we are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key

It is time to **save** your file (**File > Save as...**) or using the **save** icon in the tool bar. You can save it under the same file created in the previous example named *Corrosion Rates*.

Analyzing the Results

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

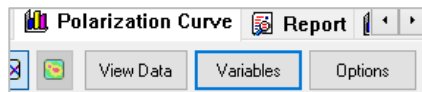
Go to the **Calculated Rates** table



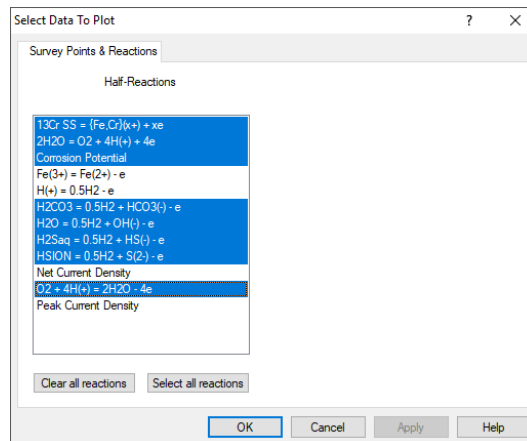
The corrosion rate of Super 13%Cr is several orders of magnitude lower when compared to the corrosion rate for Carbon Steel, i.e. at 0.0012 mm/year for 13%Cr vs 0.7 mm/year for Carbon Steel. This is consistent with the use of Super 13% Cr to protect against CO₂ corrosion.

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

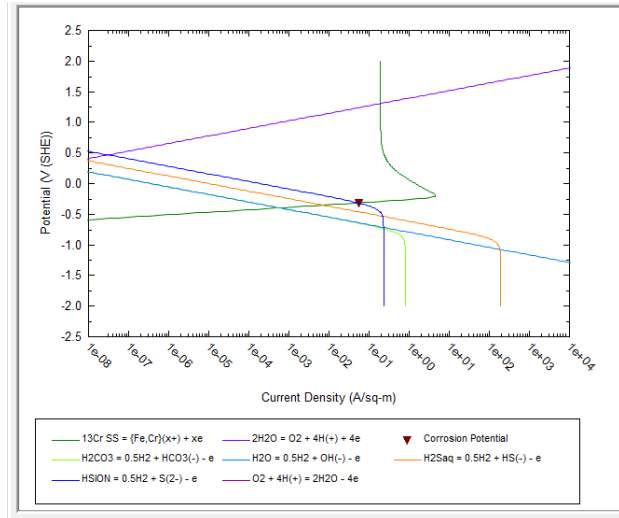
Click on the **Variables** button. This will open a new window.



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



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



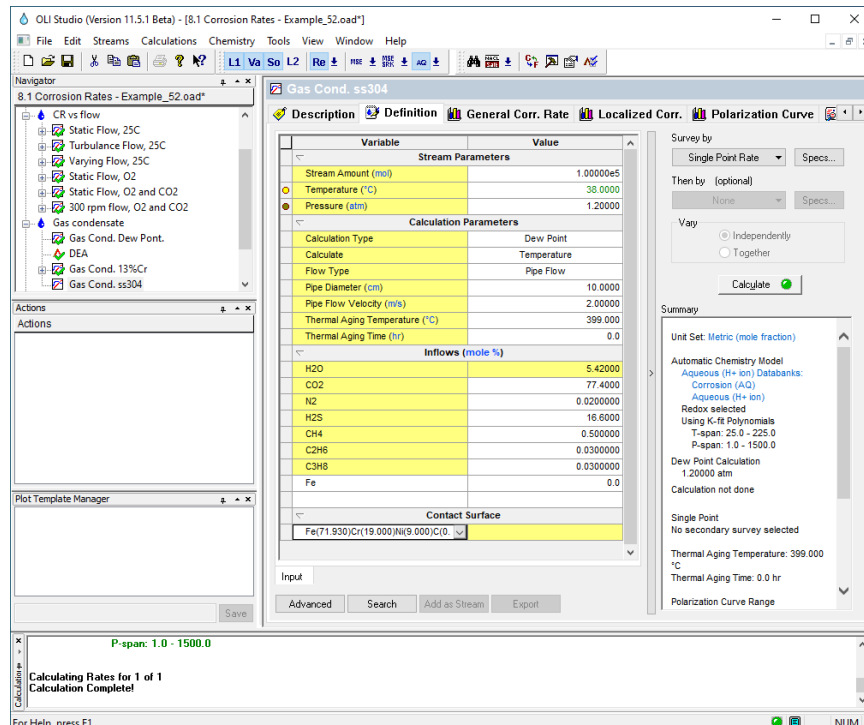
The layout of the plot was changed for easy reading. To change layout, you can right click on any part of the plot and select the option *Alloy Layout Changes* to modify the appearance of your plot.

The corrosion potential of Super 13%Cr is -0.25 V vs SHE and the corresponding corrosion current $i_{\text{corr}}=0.001\text{A/m}^2$. The i_{corr} for Carbon Steel was 0.61A/m^2 , this means that 13%Cr is 10x more resistant to corrosion under the same conditions.

Stainless Steel 304

Copy 'Gas Cond. Dew Point' corrosion calculation, and paste it under the stream 'Gas Condensate'
 Change the name to **Gas Cond. SS304** using the <F2> key
 Change the **contact surface** to Stainless Steel 304

Your screen should look like the image below.



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

Analyzing the Results

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

Go to the **Calculated Rates** table

Calculated Rates

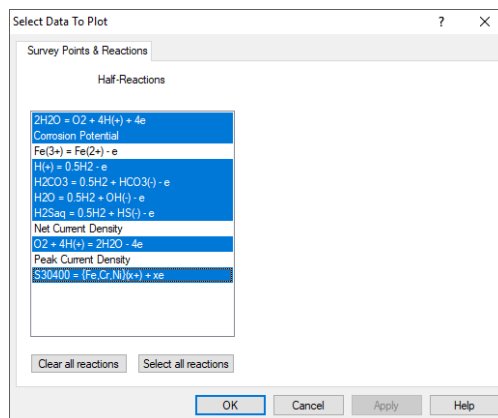
Corrosion Rate	2.40183e-3	mm/yr
Corrosion Potential	-0.293505	V (SHE)
Repassivation Potential	>2.0	V(SHE)
Corrosion Current Density	2.21614e-3	A/sq-m

The corrosion rate of 304 SS is now 0.0024 mm/year. This is a negligible value.

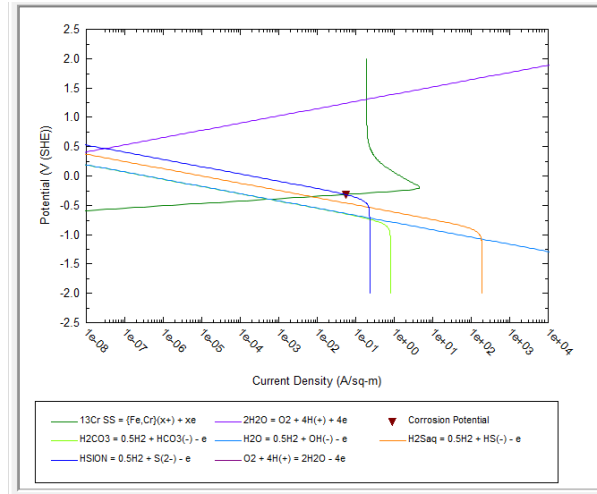
Click on the **Polarization Curve** tab ( Polarization Curve).

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

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



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



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

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

Section 9. Thermal Aging and Variations in Alloy Composition

Overview and Basic Terminology

Localized corrosion of engineering alloys is a complex function of metallurgical factors and environmental conditions. Among metallurgical factors, effects of thermal instabilities are of interest for assessing the performance and expected service life of industrial components fabricated from nominally corrosion-resistant stainless steels and nickel-base alloys.

Fabrication processes such as heat treatment and welding are known to introduce microstructural changes that may affect both the mechanical and corrosion performance of an alloy. In particular, thermal instability of stainless steels and nickel-base alloys may lead to the formation of complex metal carbides of the type M_3C_2 , M_7C_3 , M_6C , or $M_{23}C_6$ in which the metallic component M represents Cr, Mo, W, and Fe. The carbide is chromium- or molybdenum-rich depending on the carbide type, which in turn depends on the alloy composition and temperature. Also, various chromium-rich intermetallic phases can form in many alloys. Precipitation of such phases may occur at temperatures ranging from 500 to 900 °C depending on alloy composition. Formation of grain boundary carbides often results in the depletion of chromium and, possibly, molybdenum in the vicinity of the grain boundary because of the slow diffusion of substitutional elements such as chromium relative to the interstitial carbon.

Similarly, the corrosion resistance of welded components may be affected by the segregation of alloying elements and precipitation of intermetallic phases, carbides or nitrides in the solidified weld and unmixed zones as well as the precipitation of carbides and other phases in the heat-affected zone adjacent to the weld.

Sensitization of Fe-Ni-Cr-Mo alloys and its effects on intergranular attack and intergranular stress corrosion cracking is the most directly observed effect of Cr depletion. It may result in intergranular attack and intergranular stress corrosion cracking. Localized corrosion can be also affected by Cr and Mo depletion.

Corrosion Analyzer contains the following technology that can help address these issues:

A grain boundary microchemistry model for predicting the chromium and molybdenum depletion in the vicinity of grain boundaries as a result of carbide formation.

An electrochemical model for calculating the repassivation potential of Fe-Ni-Cr-Mo-W alloys as a function of alloy composition and environmental conditions including temperature and concentrations of aqueous solution species.

A procedure for calculating the observable repassivation potential that corresponds to macroscopic localized corrosion by applying the electrochemical model to the depletion profiles and performing suitable integration.

More details about this technology are described by Anderko et al. (2008), Tormoen et al. (2009), Anderko et al. (2009), and Sridhar et al. (2009).

Alloy Chemistry

Simulations can be performed, in general, for alloys that belong to the Fe-Ni-Cr-Mo-W-N-C family (i.e., for stainless steels and nickel-base alloys).

Depletion profiles in the vicinity of grain boundaries and depletion parameters can be obtained for austenitic alloys (including stainless steels and Ni-base alloys). Also, the effect of Cr and Mo depletion on localized corrosion can be calculated. This effect can be examined using the repassivation potential, which provides a threshold potential for the stabilization of localized corrosion (Anderko et al., 2009).

For other alloys from the Fe-Ni-Cr-Mo-W-N-C family, the repassivation potential can be calculated if the alloy composition is known. This also includes experimental alloys and separate phases that may be formed as a result of various forms of heat treatment (Sridhar et al., 2009).

Calculation types

Thermal aging is an additional phenomenon that can be simulated within the framework of corrosion kinetics. All calculation types and, in particular, survey types, that are supported for corrosion kinetics are also supported in conjunction with the study of thermal aging.

If it is desired to make calculations on a thermally aged sample, the thermal aging temperature and time need to be specified in the **Calc Parameters** section in the **Definition** tab. The default values are 399 °C for the thermal aging temperature and 0.0 hours for the thermal aging time. If either of these default values is used, no thermal aging effects will be predicted. Thus, by default, Corrosion Analyzer performs calculations on samples that have not been thermally aged.

Thermal Aging Temperature Survey

This calculation makes it possible to vary the thermal aging temperature within a certain range. A fixed value of thermal aging time is assumed as specified by the user. Typically, the temperatures for which thermal aging effects can be observed range from ~500 °C to ~900 °C, with the effects being most pronounced in the middle of this range.

Thermal Aging Time Survey

This calculation can be used to examine the effect of aging time at a fixed thermal aging temperature.

Output Specific to Thermal Aging

The following output can be generated:

Chromium and molybdenum depletion profiles, i.e., the variation of Cr and Mo concentration within the grain as a function of grain boundary.

The depletion parameter, which provides compact information on the extent to which the depletion process reduces the grain boundary concentration below a certain critical value of, which can be defined by well-known criteria for maintaining passivity (e.g. $x_{Cr}^* = 0.11$ or 0.12). This parameter can be calculated as the area of the depletion profile below the threshold concentration x_{Cr}^* , divided by bulk Cr concentration, x_{Cr}^0 :

$$\delta(x_{Cr}^*) = \frac{1}{x_{Cr}^0} \int_0^{z^*} (x_{Cr}^* - x_{Cr}(z)) dz$$

where z^* is the distance from the grain boundary that corresponds to the threshold concentration x_{Cr}^* .

The repassivation potential, which is a key parameter for determining whether localized corrosion can occur, may be affected by thermal aging in a rather complex way.

Thermal Aging and Variations in Alloy Composition

We will show examples of simulating the effects of thermal aging on Fe-Ni-Cr-Mo-W-C-N alloys (i.e., stainless steels and nickel-base alloys). Specifically, we will show how to predict:

Chromium and molybdenum depletion profiles in the vicinity of grain boundaries, which result from heat treatment of austenitic alloys.

Depletion parameters for sensitized austenitic alloys, which provide an indicator of whether the alloy is susceptible to intergranular corrosion.

Effect of thermal aging on the repassivation potential of austenitic alloys, which provides a threshold condition for localized corrosion (pitting or crevice corrosion).

The repassivation potential of alloys with compositional variations that may or may not result from thermal aging. This facility can also be used for bulk alloys that are not in the database or to hypothetical or experimental alloys as long as they belong to the Fe-Ni-Cr-Mo-W-C-N family. An example will be given for a duplex alloy, either annealed or thermally treated.

Example 53: Thermal aging of alloy 600

We will be studying the behavior of thermally aged alloy 600 in a dilute aqueous solution of sodium chloride, and will simulate how the time of thermal aging affects alloy 600 at a fixed thermal aging temperature of 700°C.

Starting the Simulation

Thermal Aging Calculation

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.

Thermal Aging Calculation			
Calculation Settings		Stream Composition and Conditions	
Stream Name	Thermal Aging	Stream Amount	Calculated
Calculation Type	Corrosion Rates	Temperature	60 °C
Survey by	Thermal Aging Time	Pressure	1 atm
Name Style	Display Name	H2O	Default – 55.5082 moles
Unit Set	Metric, Batch, Moles	NaCl	0.04 moles
Framework	AQ		

Add a new **Stream**

Click on the new Stream and press **<F2>** to change the name to *Thermal Aging*

Select the AQ thermodynamic Framework (selected by default)

Click on the **Units Manager** Icon and select Metric, Batch, Moles

Click on the **Names Manager** Icon and select *Display Name*

Enter the stream composition and conditions specified in the table above

Go to the **Add Calculation** button and select **Corrosion Rates**

Note: Even though the thermal aging simulation facilities do not predict corrosion rates per se, they belong to the category of corrosion kinetics and, therefore, they are included in the Corrosion Rates section of the Corrosion Analyzer.

Select the Survey by **Thermal Aging Time**

Change the name from **Rates** to **Alloy 600** using the <F2> key or by **right-mouse click** on the object and select rename

Select **Alloy 600** from the **Contact Surface** grid

In the **Calculation Parameters** grid, change the default value for the **Thermal Aging Temperature** to 700°C.

Note that the default value for the **Thermal Aging Temperature** is 399 °C, which is a low value so that, in the default case, no effects of thermal aging are being calculated.

Your screen should look like the image below.

OLI Studio - [Corrosion Rates.oad*]

File Edit Streams Calculations Chemistry Tools View Window Help

Navigator
Corrosion Rates.oad*
Streams
CR of carbon steel
CR vs flow
Gas Condensate
Localized Corrosion
Thermal Aging
Alloy 600

Alloy 600
Description Definition General Corr. Rate Localized Corr. Polarization Curve Report

Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5482
Temperature (°C)	60.0000
Pressure (atm)	1.00000
Calculation Parameters	
Flow Type	Static
Thermal Aging Temperature (°C)	700.000
Thermal Aging Time (hr)	
Inflows (mol)	
Water	55.5082
Sodium chloride	0.0400000
Nickel	0.0
Contact Surface	
Alloy 600	

Survey by
Thermal Aging Time Specs...

Then by (optional)
None Specs...

Vary
 Independently
 Together

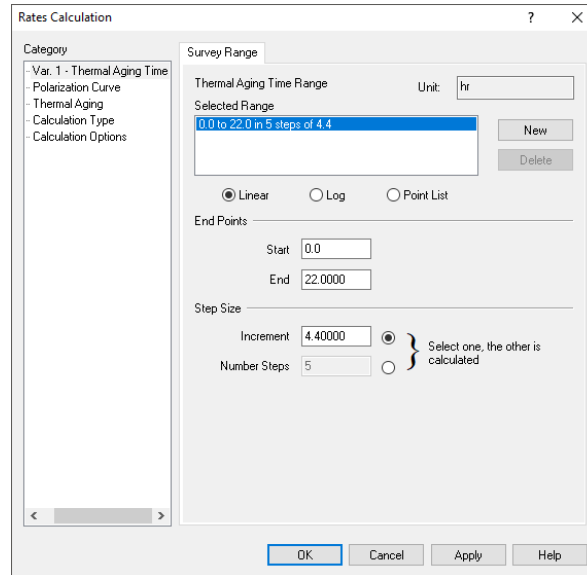
Calculate

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
Isothermal Calculation
60.0000 °C 1.00000 atm
Calculation not done
Thermal Aging Time survey:
Range 0.0 to 10.0 hr
Step size 2.0 hr
No. steps 5

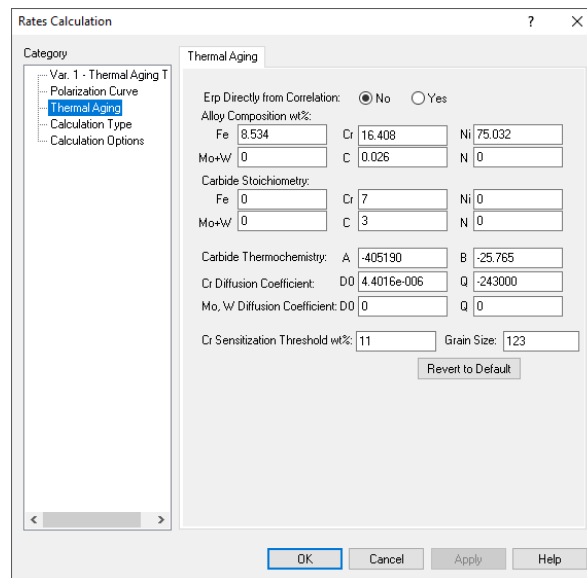
For Help, press F1

Now we need to specify the Thermal Aging Time range. **Click** on the **Specs** button. This will open a new window.

Under the **Survey Range** tab, change the range for Thermal Aging Time from 0 to 22 hours with an increment of 4.4 hours (of 5 steps).



Under the **Category** section, select the **Thermal Aging** option.



In this **Thermal Aging** Category, you can change all parameters that are necessary for calculating chromium and (if applicable) molybdenum depletion profiles. You can change:

The alloy composition (for example, to analyze the effect of a different carbon content);

The stoichiometry of the carbide phase that may form at the grain boundary; the typical carbide stoichiometry is M_7C_3 or $M_{23}C_6$ (where $M = Cr, Mo$) but can be adjusted

The parameters that define the equilibrium constant for the formation of the carbide

The diffusion coefficient of Cr and, if applicable, Mo

The threshold concentration of Cr for sensitization. This threshold concentration is used for calculating the depletion parameter.

The average grain size, which affects the process of healing of chromium depletion as a function of time


Also, you can indicate whether the repassivation potential (E_{rp}) should be calculated directly from the correlation developed by Anderko et al. (2008), which expresses E_{rp} as a function of alloy composition or not. If it is not calculated directly, then the repassivation potential is calculated first using the alloy-specific parameters for the alloy of interest and only the decrement of E_{rp} (i.e., $E_{rp, \text{thermally aged}} - E_{rp, \text{bulk alloy}}$) is obtained from the correlation. This decrement is then added to the alloy-specific E_{rp} value. This option is set by default to “No” because this maximizes the accuracy of calculations for alloys that are already in the database.

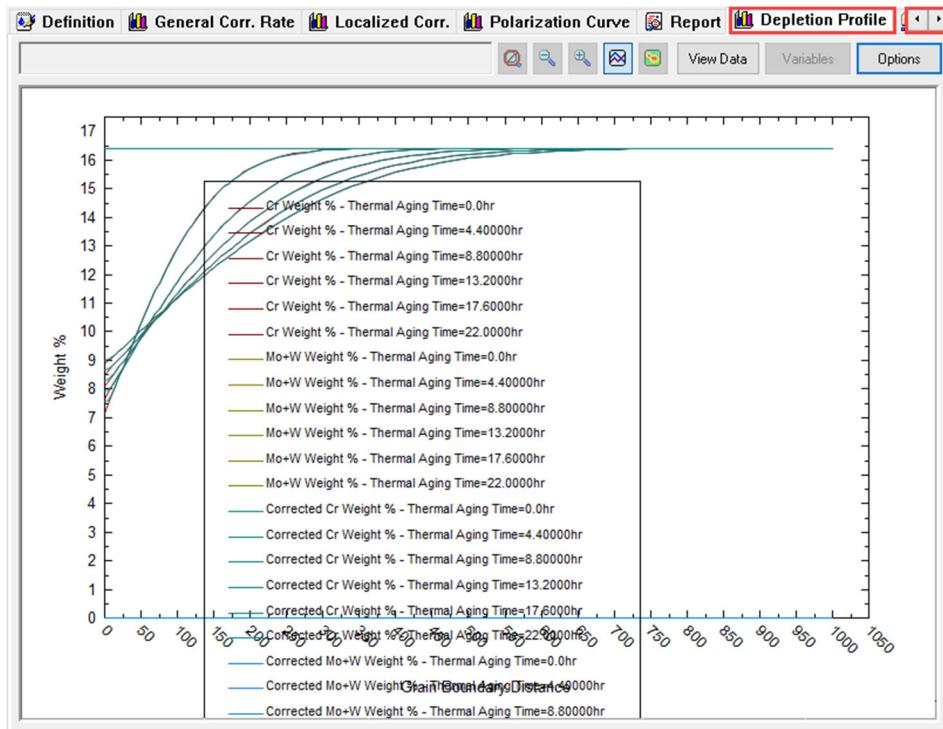
For now, we will accept the default settings. Click **OK**.

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

It is time to **save** your file (**File > Save as...**) or using the **save** icon in the tool bar. You can save it under the same file created in the previous section named *Corrosion Rates*.

Analyzing the Results

Click on the **Depletion Profile** tab ( **Depletion Profile**). If you don't see it in your screen, use the **◀▶** buttons to move the tabs.



Note: Since alloy 600 does not contain any molybdenum, the molybdenum curves will always be equal to zero.

This plot will show the concentrations of chromium and molybdenum within a grain as a function of the distance from the grain boundary (in μm). You will see that, for each condition, there are four lines:

Cr weight %: concentration of Cr in weight %

Mo+W weight %: sum of the concentrations of molybdenum and tungsten in weight %

Corrected Cr weight %: concentration of Cr corrected for beam scattering and related effects so that it can be directly compared with experimental results. The procedure for calculating the correction is described by Anderko et al. (2009).

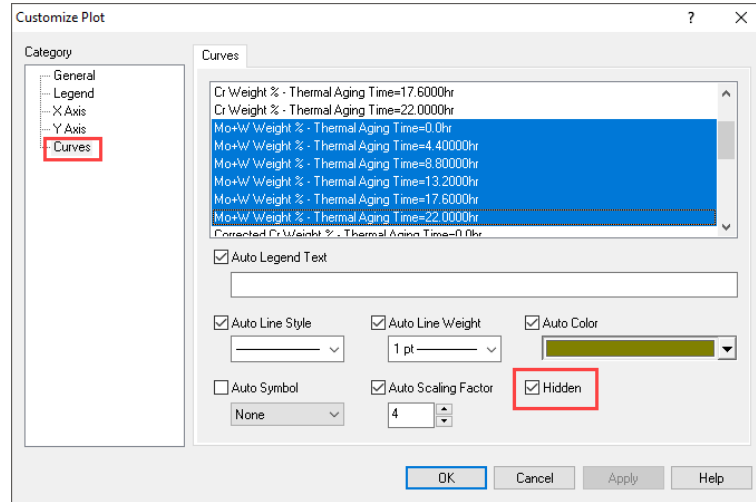
Corrected Mo+W weight %: sum of the concentrations of Mo and W corrected in the same way as those for Cr.

Let's customize the plot

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

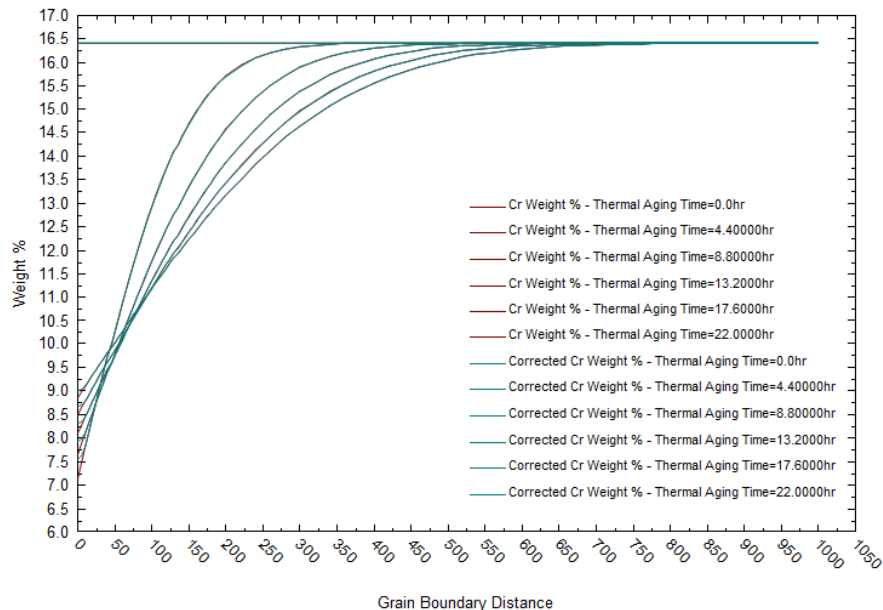
Since alloy 600 does not contain Mo or W, eliminate the Mo+W curves. To do this, go to the **Category** section and select the **Curves** option

Highlight the Mo+W weight % curves by pressing the Shift key and the down key (**Shift + ↓**). After highlighting these curves, check the **Hidden** button.



After hiding the Mo+W weight % curves, do the same for the Corrected Mo+W weight % curves. Then click **OK**.

The plot should look like the image below.



The legend of this plot was modified for clarity. The border style of the legend was modified by double clicking on the legend, and selecting *None* as the Border Style

Differences between Uncorrected and Corrected Depletion Profiles

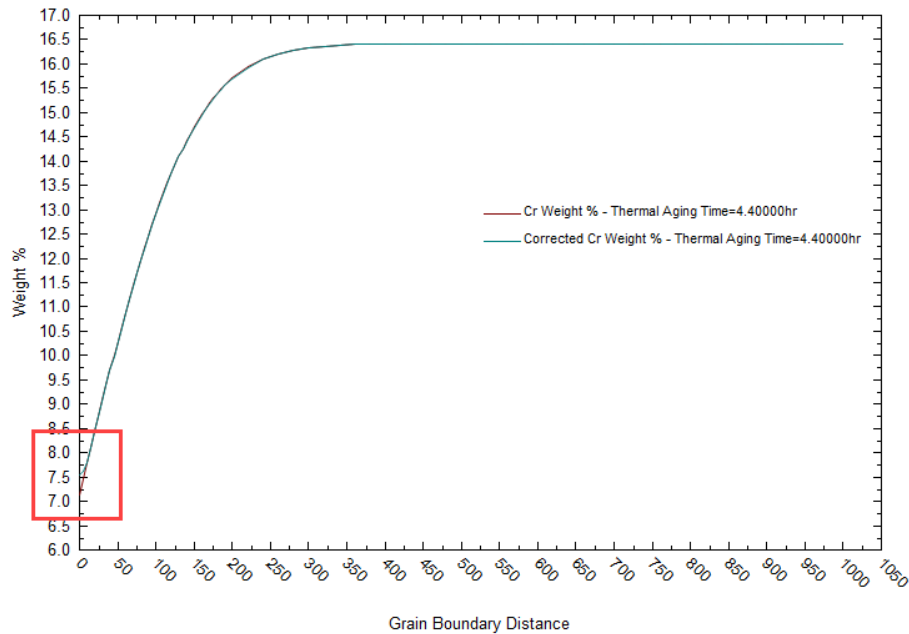
Now, let's focus on the differences between the uncorrected and corrected depletion profiles. To have a clear picture of the difference between them, we will analyze the depletion profiles results obtained at 4.4 hours of thermal aging.

Click on the **Options** button, and select the **Curves** category
Highlight all curves except the ones labeled as:

Cr Weight % - Thermal Aging Time = 4.40000 hr, and
Corrected Cr Weight % - Thermal Aging Time = 4.40000 hr

Check the **Hidden** box, then click **OK**.

Your plot should look that the image below.



In the obtained plot, you can see the difference between the two curves for small distances from the grain boundary (roughly below 30 μm). The corrected concentration is much more rounded in the vicinity of the minimum because instrumental measurement effects. At larger distances from the grain boundary, there is no difference between the two curves.

Effect of Cr depletion on corrosion

After analyzing the depletion profiles, let's focus on the effects of Cr depletion on corrosion. We will do it by analyzing two parameters – the depletion parameter and the repassivation potential.

To have more meaningful results, let's expand the range of thermal aging time and reduce the interval for calculations.

Copy the Alloy 600 corrosion calculation, and then **paste** it under the **Thermal Aging Stream**

Rename the new calculation as **Alloy 600 – Cr depletion**

Go back to the **Definition** tab and click the **Specs** button

In the **Var.1 Thermal Aging Time** category, change the Survey Range as follows: **Start=0** hours, **End= 60** hours with an **Increment= 1** hour. Then click **OK**.

Your screen should look like the image below

The screenshot shows the OLI Studio interface for defining a corrosion calculation. The main window is titled "Alloy 600-Cr depletion" and is in the "Definition" tab. The "Specs" button is highlighted in the "Thermal Aging Time" category. The "Calculate" button is highlighted in the summary panel. The summary panel shows the following details:

Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5482
Temperature (°C)	60.0000
Pressure (atm)	1.00000
Calculation Parameters	
Flow Type	Static
Thermal Aging Temperature (°C)	700.000
Thermal Aging Time (hr)	
Inflows (mol)	
Water	55.5082
Sodium chloride	0.0400000
Contact Surface	
Alloy 600	


Summary:

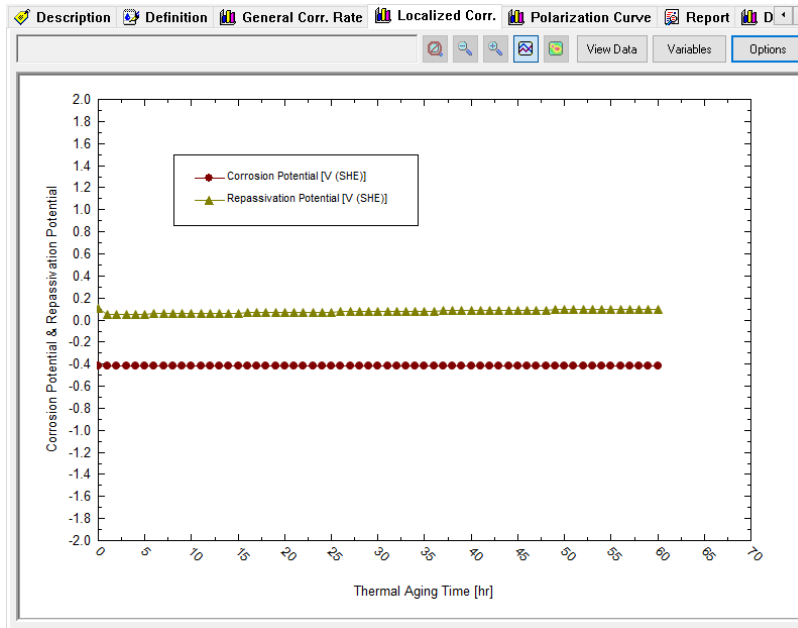
- Unit Set: Metric (moles)
- Automatic Chemistry Model: Aqueous (H+ ion) Databanks: Corrosion (Aq), Aqueous (H+ ion)
- Redox selected
- Using K-fit Polynomials
- T-span: 25.0 - 225.0
- P-span: 1.0 - 1500.0
- Isothermal Calculation: 60.0000 °C 1.00000 atm
- Calculation not done
- Thermal Aging Time survey: Range 0.0 to 60.0 hr, Step size 1.0 hr, No. steps 60
- No secondary survey selected
- Thermal Aging Temperature: 700.000 °C

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 section named *Corrosion Rates*.

Analyzing the Results

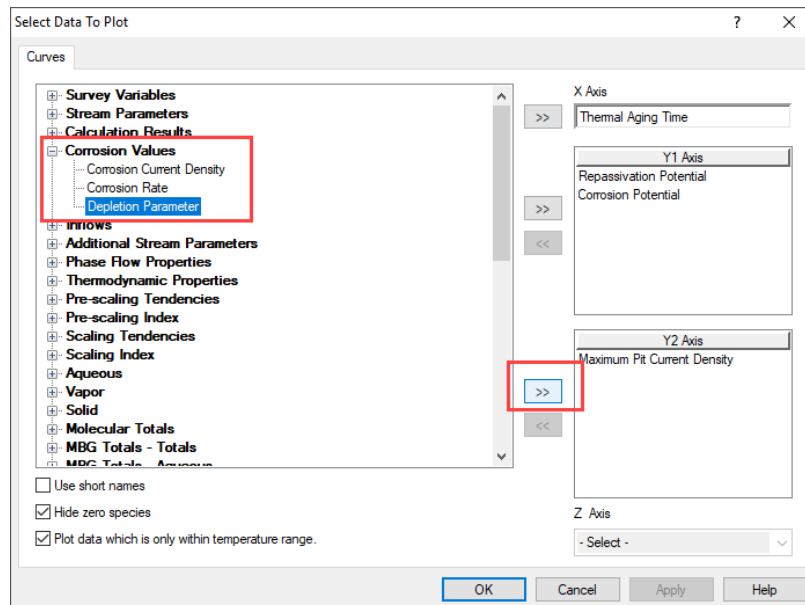
Click on the **Localized Corr.** tab ( Localized Corr.). By default, this tab will show a plot of the corrosion potential and repassivation potential.



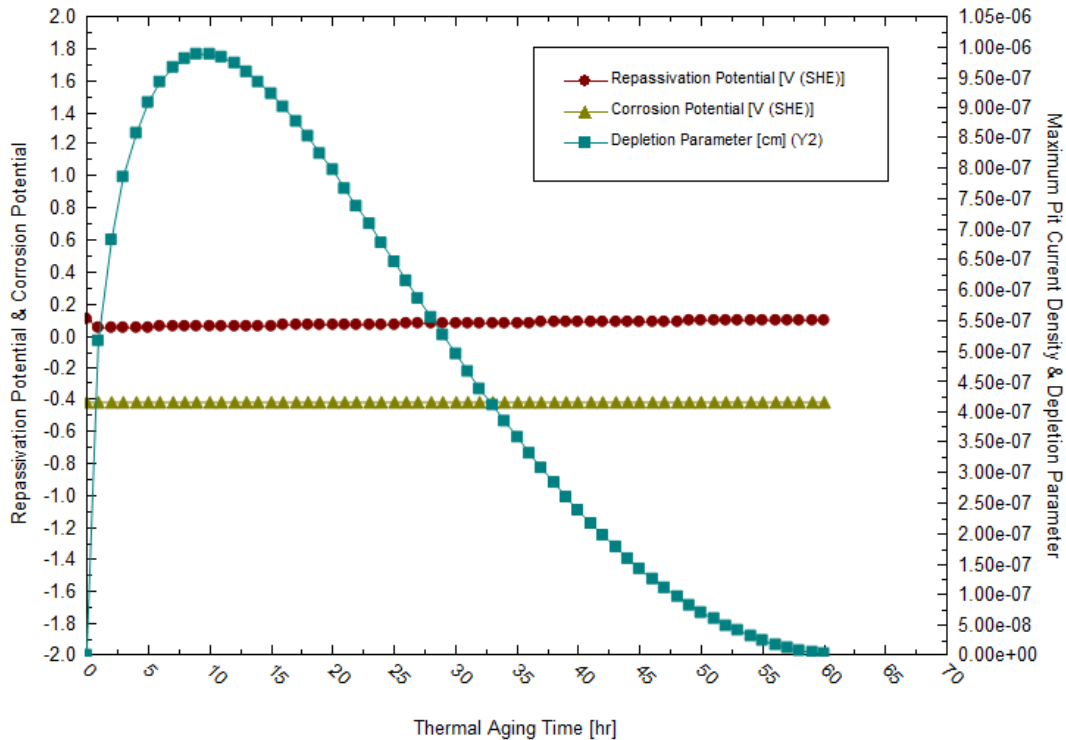
Let's add a new parameter to the plot: The **Depletion Parameter**.

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

Look for the **Corrosion Values** section, click on the '+' icon, and select the **Depletion Parameter** option. Click on the >> button that belongs the **Y2 Axis**. This action will place the new variable under the Y2 Axis. Then click **OK**.



The plot should look like the image below.



It is clear that the depletion parameter reaches a maximum for aging time of about 10 hours. Since the depletion parameter is a measure of the susceptibility of an alloy to intergranular corrosion, we can expect that the alloy will be most susceptible to intergranular corrosion at intermediate aging times. When the depletion parameter is zero, intergranular corrosion or intergranular stress corrosion cracking are unlikely. The decrease of the depletion parameter as a function of time is a manifestation of the phenomenon of healing of Cr depletion.

The repassivation potential shows a minimum as a function of aging time (see the option **View Data**). This indicates that the tendency of the alloy to undergo localized corrosion is enhanced as a result of thermal aging. However, the effect of thermal aging on the repassivation potential of alloy 600 is small (cf. Tormoen et al., 2009, Anderko et al., 2009). The repassivation potential shows a minimum at low aging times (ca. 1-2 hours). Therefore, the susceptibility to localized corrosion is enhanced the most for these aging times. It is noteworthy that the maximum in the depletion parameter does not coincide with the minimum in the repassivation potential. This is due to the fact that intergranular corrosion (which is related to the depletion parameter) and localized corrosion (which is controlled by the repassivation potential) are subject to different mechanisms. A general discussion of these differences is given by Tormoen et al. (2008).

In general, the alloy will be susceptible to localized corrosion if the corrosion potential exceeds the repassivation potential. In the above example, the corrosion potential is low because we have no oxidizing agents in the system. Therefore, the alloy will not undergo localized corrosion at the conditions of this example. However, a rise in the corrosion potential due to the presence of oxidizing agents may cause localized corrosion.

Example 54: Thermal aging of alloy 825

Alloy 825 is appreciably different from alloy 600 because it contains molybdenum and, also, substantially more chromium in addition to other alloying elements.

In this example, we will simulate how the temperature of thermal aging affects alloy 825 at a fixed thermal aging time of 15 hours.

Starting the Simulation

Thermal Aging Calculation

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.

Thermal Aging Calculation			
Calculation Settings		Stream Composition and Conditions	
Stream Name	Thermal Aging	Stream Amount	Calculated
Calculation Type	Corrosion Rates	Temperature	95 °C
Survey by	Thermal Aging Temperature	Pressure	1 atm
Name Style	Display Name	H2O	Default – 55.5082 moles
Unit Set	Metric, Batch, Moles	NaCl	2.846e-3 moles
Framework	AQ		

Under the Thermal Aging stream add a new calculation rate. Go to the **Add Calculation** button and select **Corrosion Rates** or select the **Add Corrosion Rates** icon in the **Actions panel**

Change the name from **Rates** to **Alloy 825** using the <F2> key or by **right-mouse click** on the object and select rename

Select the Survey by **Thermal Aging Temperature** option

Change the stream composition and conditions to the specified values in the table above

Select **Alloy 825** from the **Contact Surface** grid

In the **Calculation Parameters** grid, change the default value for the **Thermal Aging Time** to 15 hours

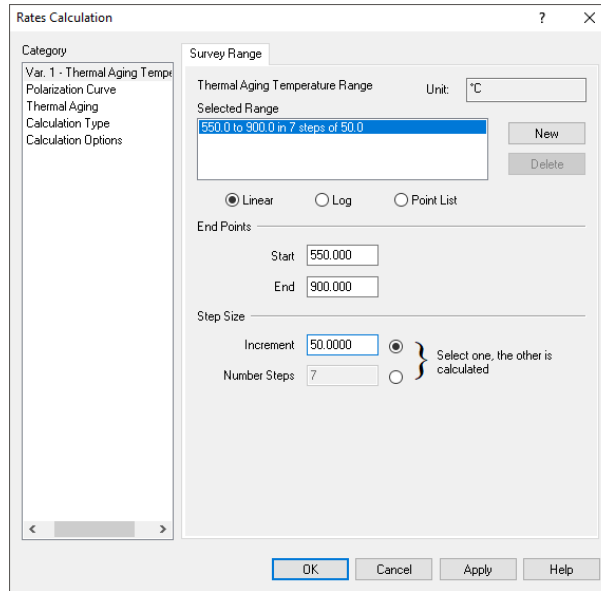
Note that the default value for the **Thermal Aging Temperature** is 0 hours, which means that no thermal aging is considered by default.

Your screen should look like the image below

The screenshot shows the software interface for the Alloy 825 simulation. The main window displays the 'Alloy 825' stream configuration. The 'Stream Parameters' section includes Stream Amount (55.5111 mol), Temperature (95.0000 °C), and Pressure (1.00000 atm). The 'Calculation Parameters' section includes Flow Type (Static), Thermal Aging Temperature (95.0000 °C), and Thermal Aging Time (15.0000 hr). The 'Inflows (mol)' section lists Water (55.5082), Sodium chloride (2.84600e-3), and Nickel (0.0). The 'Contact Surface' section lists Alloy 825. The right-hand side shows the 'Survey by' dropdown set to 'Thermal Aging Temp.' and 'Then by' set to 'None'. A 'Calculate' button is visible at the bottom right.


Now we need to specify the Thermal Aging Temperature range. **Click** on the **Specs** button. This will open a new window.

Under the **Survey Range** tab, change the range for **Thermal Aging Temperature** from 550 to 900 °C with increments of 50 °C. We will keep the other parameters at their default values. **Click OK**.

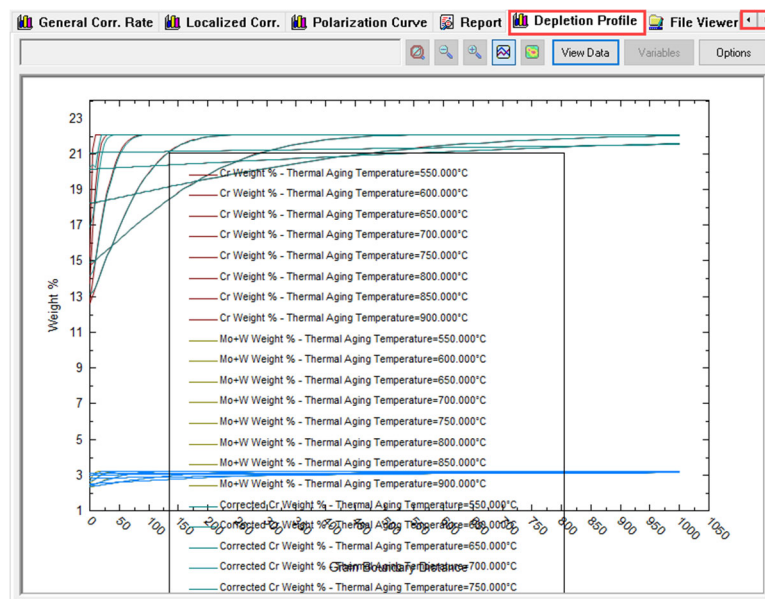


We are now ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key. It is time to **save** your file (**File > Save as...**) or using the **save** icon in the tool bar. You can save it under the same file created in the previous section named *Corrosion Rates*.

Analyzing the results

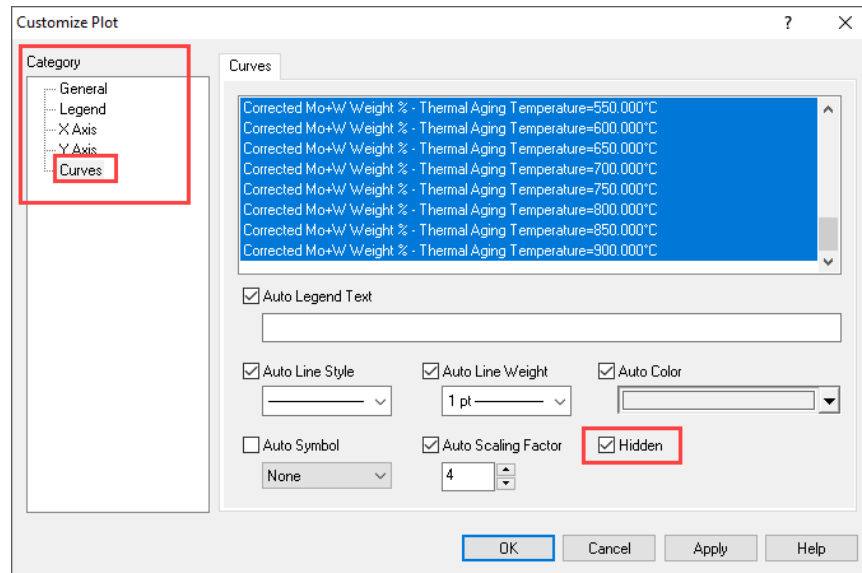
Click on the **Depletion Profile** tab ( **Depletion Profile**). If you don't see it in your screen, use the **◀▶** buttons to move the tabs.

Since alloy 825 contains Mo in addition to Cr, you will see the depletion profiles for both Cr and Mo.

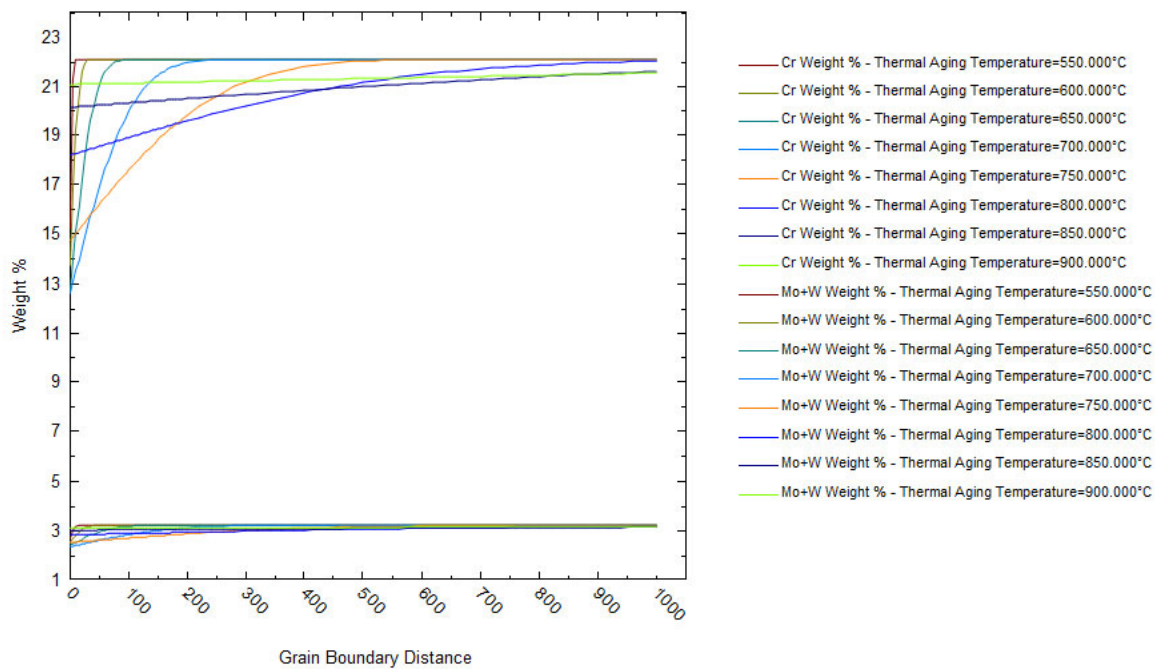


For clarity, let's customize the plot by removing the corrected depletion profiles and leaving only the uncorrected (or directly calculated) ones.

Click on the **Options** button, and select the **Curves** category, highlight the Corrected curves and check the hidden box. Then click **OK**.



Your plot should look like the image below




The plot was modified by right clicking on it and selecting the option *Allow Layout Changes*. This option allows to move and rearrange the plot and legend. Additionally, the color of the lines was changed for each temperature in order to distinguish the temperature effect.

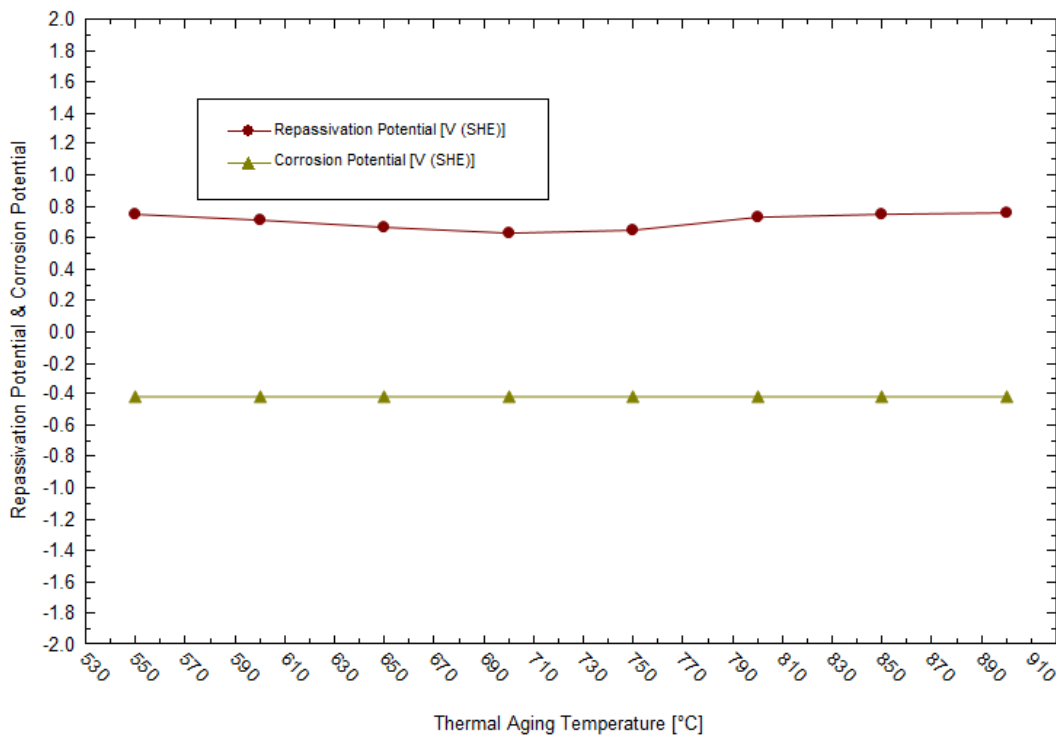
As shown in the plot above, the depletion profile is very narrow at the lowest temperature, i.e., 550 °C. On the other hand, it becomes flat at high temperatures, and it has a high minimum. The high minimum value is particularly important because it indicates that the local depletion of Cr and Mo is much less severe at high temperatures (due to much faster diffusion of substitutional elements and subsequent healing).

It should be noted that the Mo profile qualitatively parallels the Cr profile but has somewhat different slopes because of differences in diffusion coefficients of Cr and Mo.

Effect of Cr and Mo depletion on corrosion

To look at the effect of Cr and Mo depletion on corrosion

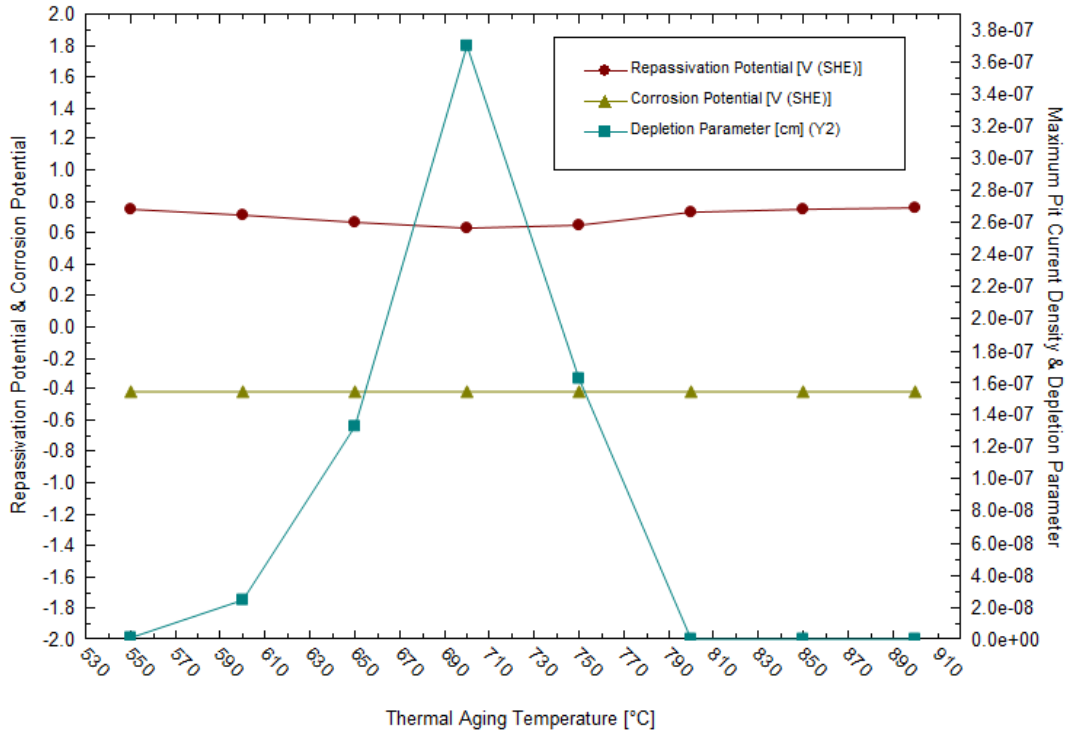
Click on the **Localized Corr.** tab ( Localized Corr.). By default, this tab will show a plot of the corrosion potential and repassivation potential.



Let's add a new parameter to the plot: The **Depletion Parameter**.

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

Look for the **Corrosion Values** section, click on the '+' icon, and select the **Depletion Parameter** option. Click on the >> button that belongs the **Y2 Axis**. This action will place the new variable under the Y2 Axis. Then click **OK**.



It is evident that both the depletion parameter and repassivation potential show their extreme values at intermediate temperatures of thermal aging. In the case of the depletion parameter, it is a maximum and, in the case of the repassivation potential, it is a minimum. This is in agreement with experimental data (Anderko et al., 2009). Non-zero values of the depletion parameter indicate the possibility of intergranular corrosion. A depression in the repassivation potential indicates an increased tendency for localized corrosion.

Thermal Aging and Localized Corrosion of Annealed and Thermally Aged Duplex Alloy 2324

In the previous examples, we used the Corrosion Analyzer's capabilities to predict the Cr and Mo depletion profiles for austenitic stainless steels and nickel-base alloys. However, we are not limited to such calculations.

We can also use the Corrosion Analyzer to predict the localized corrosion behavior of other alloys and other phases, including those that are not stored in the database. This facility is based on a generalized correlation for predicting the repassivation potential of Fe-Ni-Cr-Mo-W-N alloys as a function of alloy composition (Anderko et al., 2008). This correlation can be applied to both bulk alloys that are not in the database and to phases that may result from thermal aging.

In this section, we will go through two simulations:

First, we will predict the tendency for localized corrosion for the duplex alloy 2324 in an aerated chloride solution. Alloy 2324 (a.k.a. AISI 329) is not in the database, so the repassivation potential will be calculated from the generalized correlation (Anderko et al., 2008). The corrosion potential will be calculated for a similar alloy because the corrosion potential does not differ much for many Fe-Cr-Ni-Mo alloys in the passive state in neutral solutions.

Second, we will predict the localized corrosion tendency for alloy 2324 after thermal aging. Thermal aging of duplex steels in the temperature range of 900°C to 600°C leads to the formation of various phases - χ , σ , $M_{23}C_6$ -type carbide, and secondary austenite (γ_2). The secondary austenite phase is primarily responsible for the increased tendency of the alloy for localized corrosion. This is due to a very significant depletion of chromium in the secondary austenite over relatively wide spatial areas (Sridhar et al., 2009). Since the composition of the secondary austenite cannot be predicted at present, we will use experimental microstructural data (Sridhar et al., 2009) in conjunction with the generalized correlation for the repassivation potential.

Example 55: Prediction of Localized Corrosion for Alloy 2324 Before Thermal Aging in an Aerated NaCl Solution

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.

Thermal Aging Calculation			
Calculation Settings		Stream Composition and Conditions	
Stream Name	Thermal Aging – Alloy 2324	Stream Amount	Calculated
Calculation Type	Corrosion Rates	Temperature	60 °C
Survey by	Composition	Pressure	1 atm
Name Style	Display Name	H2O	Default – 55.5082 moles
Unit Set	Metric, Batch, Moles	NaCl	0 moles
Framework	AQ	O2	0.02 moles
		N2	0.08 moles

Note: The oxygen and nitrogen have been added to simulate the presence of air

Add a new **Stream**

Click on the new Stream and press **<F2>** to change the name to *Thermal Aging – Alloy 2324*

Select the AQ thermodynamic Framework (selected by default)

Click on the **Units Manager** Icon and select Metric, Batch, Moles

Click on the **Names Manager** Icon and select *Display Name*

Enter the stream composition and conditions specified in the table above

Go to the **Add Calculation** button and select **Corrosion Rates**

Select the Survey by **Composition**

Change the name from *Rates* to *Alloy 2324 – before aging* using the **<F2>** key or by **right-mouse click** on the object and select rename

Since alloy 2324 is not available in the database, we will select stainless steel 316 as the contact surface. This will ensure that the predicted corrosion potential is very similar to that for alloy 2324.

Select **Stainless Steel 316** from the **Contact Surface** grid

Unlike in the previous examples, do not make any changes in the **Calc Parameters** section. We will not make Cr depletion calculations; rather, we will be specifying the **compositions of the phases**.

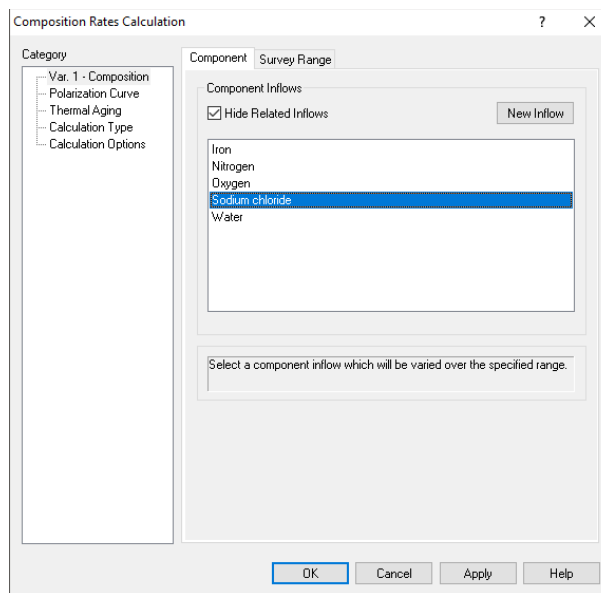
Your screen should look like the image below.

Variable	Value
Stream Parameters	
Stream Amount (mol)	55.6082
Temperature (°C)	60.0000
Pressure (atm)	1.00000
Calculation Parameters	
Flow Type	Static
Thermal Aging Temperature (°C)	399.000
Thermal Aging Time (hr)	0.0
Inflows (mol)	
Water	55.5082
Sodium chloride	0.0
Oxygen	0.0200000
Nitrogen	0.0800000
Iron	0.0
Contact Surface	
Stainless steel 316	

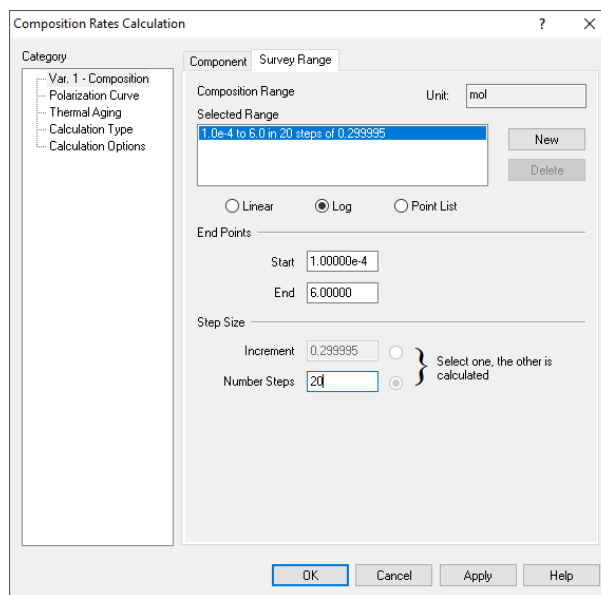
We will be running a composition survey to see how the concentration of NaCl affects the propensity for localized corrosion.

We need to specify the NaCl concentration range. Click on the **Specs** button. This will open a new window.

Under the **Component** tab select **Sodium Chloride**



Click on the **Survey Range** tab and change the concentration range as follows: Start=0.001 moles, End=6 moles, and number of steps=20. Then, click on the Log radio button.



Under the **Category** section, select the **Thermal Aging** option. The screen will be populated with default parameters for type 316 stainless steel.

In the following steps we are going to enter the alloy 2324 composition and use the repassivation potential (E_{rp}) correlation (embedded in the software) to calculate the E_{rp} of the alloy. This is necessary because no parameters for alloy 2324 are stored in the databank and we have to rely exclusively on the correlation to predict the repassivation potential.

First, click on the **Yes** button next to “*Erp directly from correlation:*”

Then, enter the composition of alloy 2324 by replacing the default values for alloy 316.

Enter the following composition of alloy 2324:

Element	Composition (wt%)
Fe	67.245*
Cr	25.4
Ni	5.75
Mo+W	1.5
C	0.025
N	0.08

*which is the balance that includes many minor elements

The remaining parameters in the Thermal Aging screen can remain the same because we will not be using them in this example (i.e., we will not be calculating any depletion profiles). After entering the values, the screen should look as follows:


The screenshot shows the 'Composition Rates Calculation' dialog box with the 'Thermal Aging' tab selected. The 'Erp Directly from Correlation' option is set to 'Yes'. The 'Alloy Composition wt%' section contains input fields for Fe (67.245), Cr (25.4), Ni (5.75), Mo+W (1.5), C (0.025), and N (0.08). The 'Carbide Stoichiometry' section has input fields for Fe (0), Cr (19.74), Ni (0), Mo+W (3.26), and C (6). The 'Carbide Thermochemistry' section has input fields for A (41221), B (-966), Cr Diffusion Coefficient: D0 (0.00016818), Q (-289000), Mo, W Diffusion Coefficient: D0 (7.93e-005), and Q (-274000). The 'Cr Sensitization Threshold wt%' is set to 12 and 'Grain Size' is set to 100. There is a 'Revert to Default' button and 'OK', 'Cancel', 'Apply', and 'Help' buttons at the bottom.

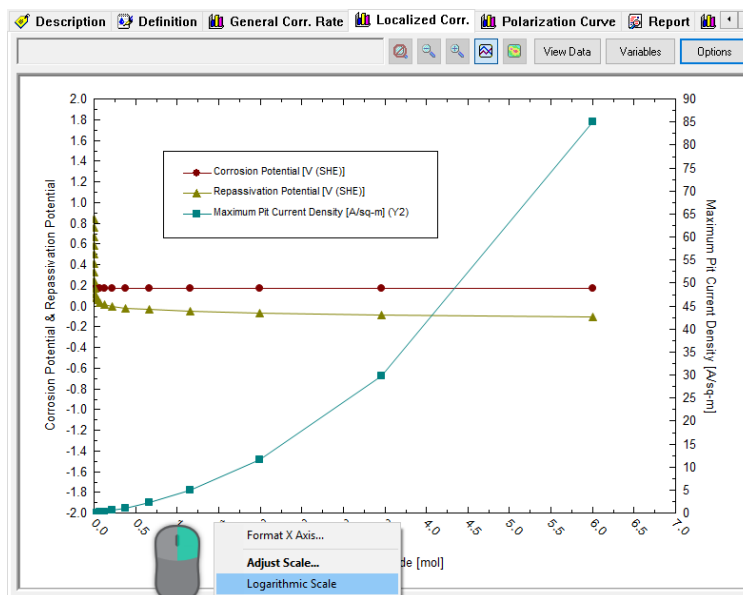
Click **OK** to accept the changes

We are now 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 section named *Corrosion Rates*.

Analyzing the results

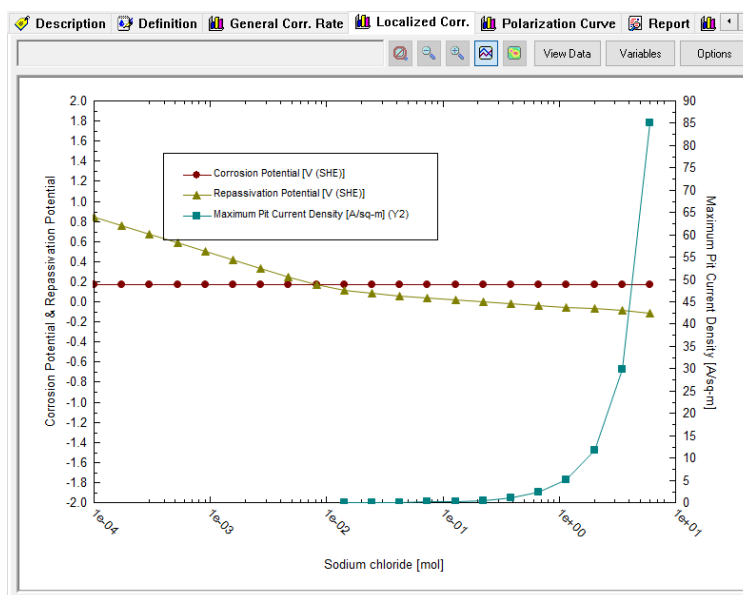
Click on the **Localized Corr.** tab ( Localized Corr.). By default, this tab will show a plot of the corrosion and repassivation potentials as a function of NaCl concentration. In the Y2 axis the Maximum Pit Current Density is also plotted.



To visualize the results better, change the horizontal axis to a logarithmic scale.

Right-mouse click on the X Axis and select **Logarithmic Scale**

The plot should look like the image below.



These results indicate that alloy 2324 is susceptible to localized corrosion in aerated solutions when the chloride concentration exceeds ~0.3 molal. Above this concentration, the repassivation potential drops below the corrosion potential and, therefore, localized corrosion can be stabilized at these conditions.

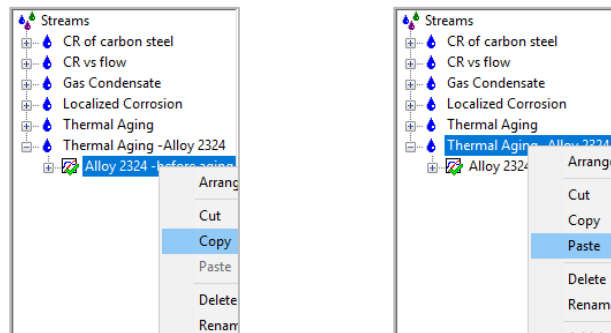
Example 56: Prediction of Localized Corrosion for Alloy 2324 After Thermal Aging

Now, we will perform the same prediction of localized corrosion calculations for thermally aged alloy 2324. We will run the same concentration survey as in the previous case so that we can compare the results for bulk alloy 2324 with those for a heat-treated sample.

Sridhar et al. (2009) found that after aging alloy 2205 at 700 °C for 24 hours, the formation of a chromium-depleted secondary austenite phase is responsible for a much-increased tendency for localized corrosion. We will use this experimental data to approximate the localized corrosion tendency of alloy 2324.

Starting the Simulation

Copy the *Alloy 2324-before aging* calculation and **paste** it under the *Thermal Aging – Alloy 2324* stream



Rename the calculation as *Alloy 2324 – after aging* by using the <F2> key or by **right-mouse click** on the object and select rename

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

Under the **Category** section, select the **Thermal Aging** option. The screen will be populated with default parameters for type 316 stainless steel.

Click on the **Yes** button next to “*Erp directly from correlation:*” – because we will be running calculations for a completely new phase

Then, enter the composition of the secondary austenite phase by replacing the default values for alloy 316.

Note: we are using experimental data obtained for alloy 2205 for illustration purposes). For more details how these compositions were determined, see the paper of Sridhar et al. (2009).

Enter the following composition:

Element	Composition (wt%)
Fe	80.774*
Cr	12.512
Ni	5.134
Mo+W	1.399
C	0.017
N	0.164

*which is the balance that includes many minor elements

The remaining parameters in the Thermal Aging screen can remain the same because we will not be using them in this example (i.e., we will not be calculating any depletion profiles). After entering the values, the screen should look like the image below.

The screenshot shows a software dialog box titled "Composition Rates Calculation" with a "Thermal Aging" tab selected. On the left, a "Category" list includes "Var. 1 - Composition", "Polarization Curve", "Thermal Aging", "Calculation Type", and "Calculation Options". The main area contains several input fields and a "Revert to Default" button. At the bottom, there are "OK", "Cancel", "Apply", and "Help" buttons. The "OK" button is highlighted with a blue border.


Parameter	Value
Alloy Composition wt%: Fe	80.774
Alloy Composition wt%: Cr	12.512
Alloy Composition wt%: Ni	5.314
Alloy Composition wt%: Mo+W	1.399
Alloy Composition wt%: C	0.017
Alloy Composition wt%: N	0.164
Carbide Stoichiometry: Fe	0
Carbide Stoichiometry: Cr	19.74
Carbide Stoichiometry: Ni	0
Carbide Stoichiometry: Mo+W	3.26
Carbide Stoichiometry: C	6
Carbide Stoichiometry: N	0
Carbide Thermochemistry: A	41221
Carbide Thermochemistry: B	-.966
Cr Diffusion Coefficient: D0	0.00016818
Cr Diffusion Coefficient: Q	-289000
Mo, W Diffusion Coefficient: D0	7.93e-005
Mo, W Diffusion Coefficient: Q	-274000
Cr Sensitization Threshold wt%	12
Grain Size	100

Click **OK** to accept the changes

We are now 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

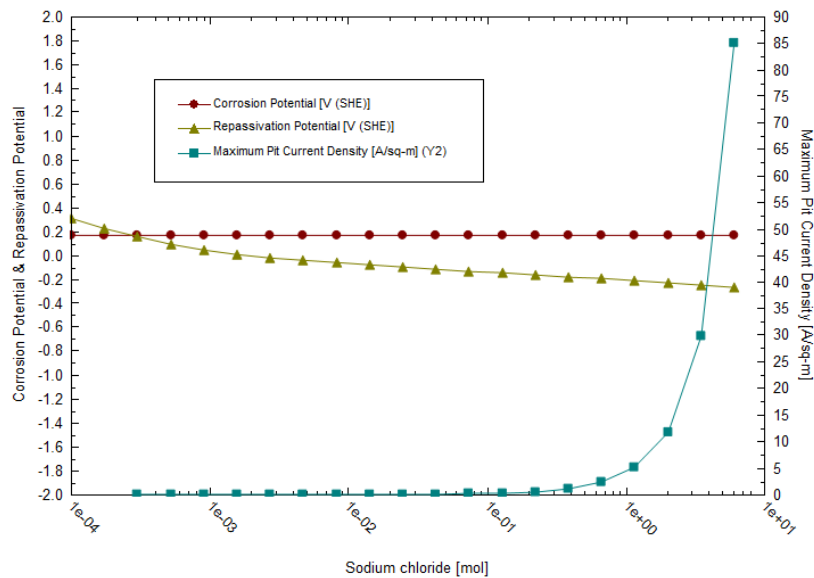
Analyzing the results

Click on the **Localized Corr.** tab ( Localized Corr.). By default, this tab will show a plot of the corrosion and repassivation potentials as a function of NaCl concentration. In the Y2 axis the Maximum Pit Current Density is also plotted.

To visualize the results better, change the horizontal axis to a logarithmic scale.

Right-mouse click on the X Axis and select **Logarithmic Scale**

The plot should look like the image below.



The obtained plot shows that the repassivation potential is much lower than that for bulk alloy 2324. Because of the strong depression of the repassivation potential, the corrosion potential exceeds the repassivation potential at chloride concentrations of ~ 0.0007 m. Thus, localized corrosion is predicted to be possible at concentrations above 0.0007 m. This indicates a very strong increase in the propensity for localized corrosion compared with bulk alloy 2324, for which the predicted threshold is ~ 0.3 m.

In general, you can use this facility to predict the repassivation potential for any alloys, including unknown and experimental ones, as long as they belong to the Fe-Ni-Cr-Mo-W-N-C family.

Chapter IV – OLI Studio: EVS Analyzer

Section 10. EVS Overview

Overview and Theoretical Foundation

Engineering systems may have many pits and corroded areas of varying degree of severity. The first perforation, whose time and location will be a matter of probability, may cause the failure of the construction. Accordingly, the probability of such failure must be known as accurately as possible.

Extreme value statistics (EVS) is one of the most powerful statistical techniques that have been used extensively to extrapolate damage (maximum pit depth) from small samples in the laboratory to larger area samples in the field (see, for example, Eldridge G. 1957, Shibata T. et al. 1988, Kowaka et al. 1994). Thus, it was shown (Shibata T. et al. 1988) that probability of failure of a construction, P_f , i.e. the probability that at least one pit reaches the critical dimension, d , (for example wall thickness) in the system with area S is described by the equation:

$$P_f = 1 - \exp\left\{-\frac{\exp[-d-(u+\alpha \ln \frac{S}{s})]}{\alpha}\right\} \quad (1)$$

where location parameter, u , and scale parameter, α , are measured by using small samples with constant area, s . Equation (1) is to extrapolate corrosion damage from a small reference area, such as a coupon to a larger operation area, S . This is the classical use of Extreme Value Statistics.

Experimental studies demonstrate that both the shape and location parameters are time dependent. However, those dependencies must be established empirically and since no theory contained within classical EVS is available for the functional forms of $u(t)$ and $\alpha(t)$, it is necessary to know answer (prediction) in advance for predicting the damage at long times. This has proven to be a severe constrains of the applicability of classical EVS.

This problem can be overcome by applying damage function analysis (DFA) method that considers propagation of corrosion damage by drawing an analogy between the growth of a pit and the movement of a particle (Engelhardt and Macdonald, 2004). In many cases DFA yields an analytical expression for u and α in terms of time of the hyperbolic form:

$$u = \frac{a_1 t}{1+a_2 t} \text{ and } \alpha = a_3 t \quad (2)$$

where a_1 , a_2 , and a_3 are readily determined by calibration from short term data in order to predict damage over the longer time. Namely, equations (2) are used now by OLI software for predicting damage in corroding systems. It must be noted that a different (power) form of such dependencies has been used by Laycock et al. 1990.

Input and Output Specific to EVS

For applying this technique the user has to provide a set of experimental data (x_i, t_i, s_i) , $i = 1, 2, \dots, N$, where x_i is the depth of the deepest pit over area s_i , of a metal exposed to corrosion attack. The separate area, s_i , could be distinct coupons from a designed experiment or random samples at various times from different locations in the system. Experiments must be performed for at least two different times.

The output of the code yields the probability of failure as a function of time for a large system with area S . The code also allows the user to answer on several engineering questions, for example, what service life, t , will have the pipe with the width, d , and length L in order to ensure acceptable performance (probability of failure, P_f).

Advantages and Disadvantages of EVS

The advantage of this approach is self-evident. The prediction of corrosion damage for long times will be done by using experimental data for short times without requiring the explicit determination of any information about the kinetic parameters of the system. However, such approach has evident disadvantages, as follows:

The results of the analysis cannot be transferred for predicting corrosion damage to other systems (for example pipelines) due to the different technological and environmental conditions that generally exist. The results cannot be used for predicting damage in the same system if technological and environmental conditions change.

We can expect that when the depth of the pit increases some critical value, the nucleation of cracks can occur. A purely statistical method cannot predict such a transition. This method also cannot predict any catastrophic event.

This method cannot be used for design of new construction, because it relies upon calibration upon a pre-existing system.

Extreme Value Statistics for Predicting Pitting Damage

We will show examples of applications of Extreme Value Statistics for predicting pitting damage. Specifically, we will show how to predict:

The depth of the deepest pit in the engineering structure or laboratory systems as a function of time and the surface area of the system

Probability of failure for a given penetration depth and the area of the system as a function of observation time

Probability of failure for a given observation time and the area of the system as a function of penetration depth

Probability of failure for a given penetration depth and observation time as a function of the area of the system

Foundations of Extreme Value Statistics can be found in the following references: (Aziz, 1956, Kowaka et al. 1994, Laycock et al. 1990, Engelhardt and Macdonald, 2004).

Example 57: Corrosion of Aluminum Alloy in Tap Water

In this example, we will consider the classical data for pitting corrosion (Aziz, 1956). In this paper, we can find particularly the experimental data for the maximum pit depths developed on Alcan 2S-O coupons with area $\approx 129 \text{ cm}^2$ immersed in Kingston tap water at 25°C . The experimental data is summarized in the table below.

Maximum pit depth (in μm) developed on Alcan 2S-O coupons with immersed in Kingston tap water for different observation times. Area of all coupons is $\approx 129 \text{ cm}^2$

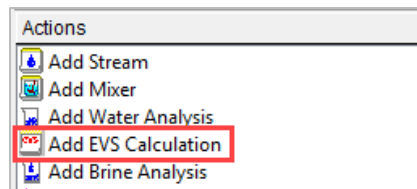
Coupon #	One Week 7 days	One Month 30 days	Three Months 90 days	Six Month 180 days	One Year 365 days
1	180	460	480	620	640
2	266	500	578	620	680
3	290	510	610	620	700
4	306	580	610	680	760
5	334	580	610	680	800

6	340	640	660	720	810
7	340	654	690	740	820
8	410	680	718	740	840
9	410	692	760	760	840
10	545	692	798	760	900

Calculating the Depth of the Deepest Pit

Starting the Simulation

Add a new **EVS** calculation. Select the **Add EVS Calculation** icon in the Actions Pane



Click on the new EVS calculation and press **<F2>** to change the name to *EVS-Aluminum samples*. Notice that the default calculation is the *Pit Depth Prediction*.

All samples have a constant area $s = 129 \text{ cm}^2$. Under the **Calculation Parameters** grid, enter 129 cm^2 for the **Surface Area** and **Default Value** cells.

The screenshot shows the OLI Studio interface with the EVS calculation setup. The main window displays the 'Description', 'Definition', 'Plot', and 'Report' tabs. The 'Calculation Parameters' table is visible, with the following data:

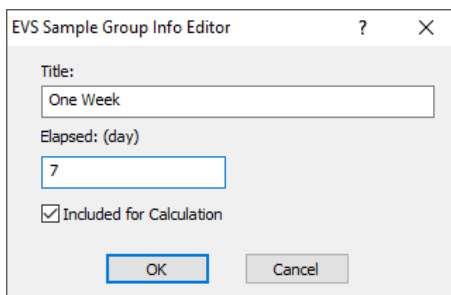
Description	Pit Depth (μm)	Area (sq-cm)
Calculation Parameters		
Surface Area		129.000
Experiment Start (day)	0	...
Default Value		129.000
Sample Group 01 (day)	7172.14	...

The 'Add Group' button is highlighted with a red box. The 'Summary' pane on the right shows the calculation type as 'Pit Depth Prediction' and the calculation parameters: Surface Area 129.000 sq-cm , Experiment Start: 01/01/2000, Range: 0.0 to 365.0 day, Step size: 5.0 day, No. steps: 73, and Default Area Value: 129.000.

There are experimental data sets for 5 different periods of time. This means that we need to enter 5 different sample groups.

By default, **Sample group 01** is created. Click on the button to edit this field. This will open a new window.

Change the title to **One Week**, enter the number **7** for the number of **elapsed days**, and **check** the box '**Include for Calculation**'. Then click **OK**.



EVS Sample Group Info Editor

Title:
One Week

Elapsed: (day)
7

Included for Calculation

OK Cancel

Enter the **Pit Depth** data (second column) obtained for 1 week

Description	Pit Depth (μm)	Area (sq-cm)
Calculation Parameters		
Surface Area		129.000
< Experiment Start (day)	0	...
Default Value		129.000
< <input checked="" type="checkbox"/> One Week (day)	7.0	...
1	180.000	129.000
2	266.000	129.000
3	290.000	129.000
4	306.000	129.000
5	334.000	129.000
6	340.000	129.000
7	340.000	129.000
8	410.000	129.000
9	410.000	129.000
10	545.000	129.000

Now we need to add 4 more groups.

Click on the **Add Group** button (located at the bottom of the window). This will open a new window.

Change the title to **One Month**, enter the number 30 for the number of **elapsed days**, and **check** the box '**Include for Calculation**'. Then click **OK**.

Enter the **Pit Depth** data (second column) obtained for 1 month.

Click on the **Add Group** button, and repeat the same procedure for one month, three months, six months and one year.

The information for this group is entered, but by un-checking the box, the information is not considered for the calculation

Description			Pit Depth (µm)	Area (sq-cm)
<input checked="" type="checkbox"/> One Month (day)			30.0	...
1			460.000	129.000
2			500.000	129.000
3			510.000	129.000
4			580.000	129.000
5			580.000	129.000
6			640.000	129.000
7			654.000	129.000
8			680.000	129.000
9			692.000	129.000
10			692.000	129.000
<input type="checkbox"/> Three Months (day)			89.9999	...
1			480.000	129.000
2			578.000	129.000
3			610.000	129.000
4			610.000	129.000
5			610.000	129.000
6			660.000	129.000
7			690.000	129.000
8			718.000	129.000
9			760.000	129.000
10			798.000	129.000
<input type="checkbox"/> Six Months (day)			180.0	...
1			620.000	129.000
2			620.000	129.000
3			620.000	129.000
4			680.000	129.000
5			680.000	129.000
6			720.000	129.000
7			740.000	129.000
8			740.000	129.000
9			760.000	129.000
10			760.000	129.000
<input type="checkbox"/> One Year (day)			365.0	...
1			640.000	129.000
2			680.000	129.000
3			700.000	129.000
4			760.000	129.000
5			800.000	129.000

Note the following:

Here, for the description of different experiments we simply used the number of the corresponding row in Table 1. However, this description can be done in an arbitrary form.

For each group, the order of samples relative depth can be arbitrary (not necessary in ascending order as in Table 1)

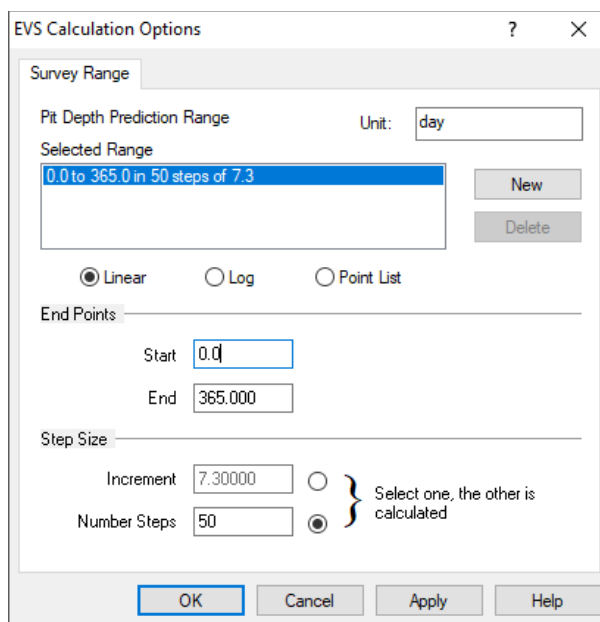
If coupons have different areas each area must be specified in the column **Area**

Radio button **Elapsed** means the time after corrosion attack is used in calculations and namely this time is used usually in scientific publication. However, it is possible to use also **Actual Time** of the experiments.

At this point, the experimental data has been entered. Now we need define the period of time for which we want to do the prediction of failure due to pitting.

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

Under the **Survey Range** tab, enter the range for **Pit Depth Prediction** as follows: Start=0 days, End=365 days, and number of steps=50. Then click **OK**



Before running the calculation, we are going to study two different cases:

The first case will include the experimental data for 1 week and 1 month – short term experiments

The second case will include all the experimental data – long term experiments

Predicting the Worst Pit Depth for 1 year of service life using short term experiments (Experimental Data for 1 week and 1 month)

Check the boxes for 1 week and 1 month only to include them into the calculations


The screenshot shows a software window with four tabs: Description, Definition, Plot, and Report. The main area is a table with three columns: Description, Pit Depth (µm), and Area (sq-cm). The table is organized into sections for different time intervals. The 'One Week (day)' section is selected with a checkmark and shows a pit depth of 7.0 µm. The 'One Month (day)' section is also selected with a checkmark and shows a pit depth of 30.0 µm. The 'Three Months (day)' and 'Six Months (day)' sections are not selected. The table contains 10 rows of data for each selected interval, showing an increasing trend in pit depth over time. At the bottom, there is an 'Add Group' button and two radio buttons: 'Elapsed' (selected) and 'Actual Time'.

Description	Pit Depth (µm)	Area (sq-cm)
Calculation Parameters		
Surface Area		129.000
Experiment Start (day)	0	...
Default Value		129.000
<input checked="" type="checkbox"/> One Week (day)	7.0	...
1	180.000	129.000
2	266.000	129.000
3	290.000	129.000
4	306.000	129.000
5	334.000	129.000
6	340.000	129.000
7	340.000	129.000
8	410.000	129.000
9	410.000	129.000
10	545.000	129.000
<input checked="" type="checkbox"/> One Month (day)	30.0	...
1	460.000	129.000
2	500.000	129.000
3	510.000	129.000
4	580.000	129.000
5	580.000	129.000
6	640.000	129.000
7	654.000	129.000
8	680.000	129.000
9	692.000	129.000
10	692.000	129.000
<input type="checkbox"/> Three Months (day)	89.9999	...
1	480.000	129.000
2	578.000	129.000
3	610.000	129.000
4	610.000	129.000
5	610.000	129.000
6	660.000	129.000
7	690.000	129.000
8	718.000	129.000
9	760.000	129.000
10	798.000	129.000
<input type="checkbox"/> Six Months (day)	180.0	...
1	620.000	129.000

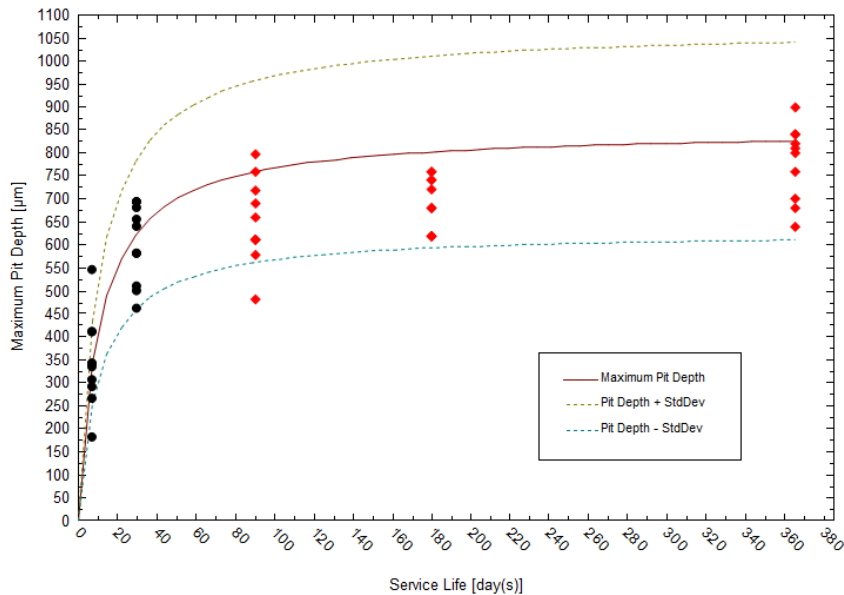
We are now ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key

It is time to **save** your file (**File > Save as...**) or using the **save** icon in the tool bar. Save this new file as *EVS calculations*.

Analyzing the results

Click on the **Plot** tab ( **Plot**). You will see a plot of the predicted mean value of the depth of the deepest pit, x_m and the plots of values $x_m - \sigma$ and $x_m + \sigma$, where σ is the standard deviation of x_m .

It is important to note that only data for short term experiments (for 1 week and 1 month) are shown as black circles in the plot. The additional data are shown as red diamonds, only for demonstrating the accuracy of prediction.



Click on the **Report** tab, and to the **Calculation Results** table.

The predicted depth of the deepest pit at 365 days is $610.43\mu\text{m} \leq 825.373\mu\text{m} \leq 1040.31\mu\text{m}$ (based on the short-term experimental data).

Predicting the Worst Pit Depth for 2 years of service life using long term experiments (all data sets)

The accuracy of prediction increases when additional group of experiments are included into consideration. For this case we are going to add the experimental data for 3 months, 6 months and 1 year.

Go back to the **Definition** tab

Include (check) the experimental data for 3 months, 6 months and 1 year

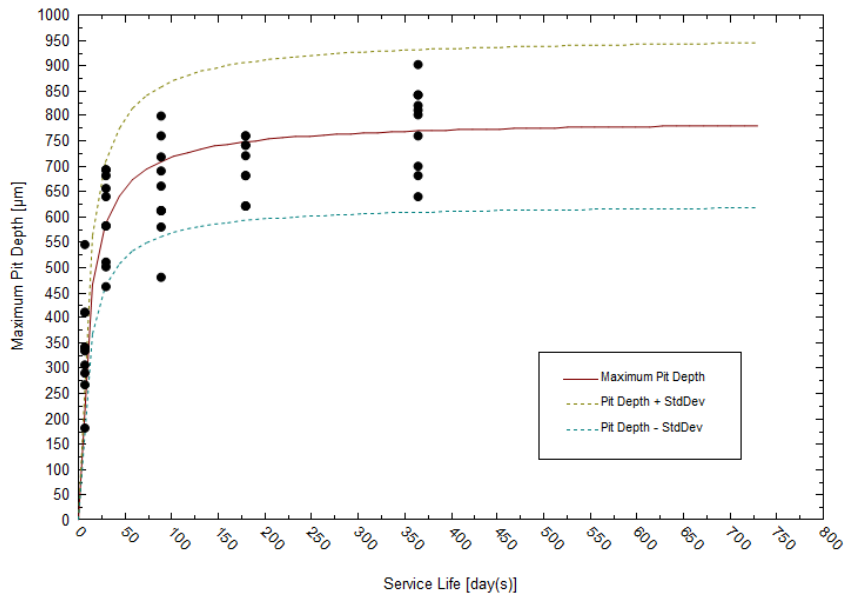
Click on the **Specs** button. This will open a new window

Under the **Survey Range** tab, enter the range for **Pit Depth Prediction** as follows: Start=0 days, End=730 days, and number of steps=50. Then click **OK**

Then **Click** on the **Calculate** button or press the **<F9>** key

Analyzing the results

Click on the **Plot** tab ( Plot).



Click on the **Report** tab, and to the **Calculation Results** table.

The predicted depth of the deepest pit at 730 days (1 year) is $617.57 \mu\text{m} \leq 780.873 \mu\text{m} \leq 944.18 \mu\text{m}$.

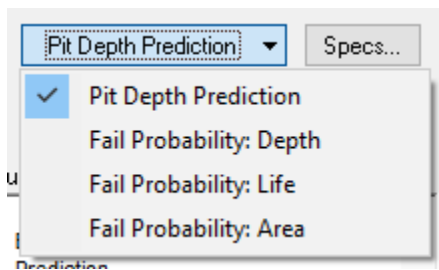
Calculating Fail Probabilities

When doing engineering design, information regarding the probability of failure is of importance to consider. The next set of calculations will involve calculating the Probability of Failure for a given:

Penetration depth

Observation time (life)

Area of the system



Fail Probability: Depth

Let's start with the calculation of Probability of Failure for a given penetration depth and the area of the system as a function of observation time.

We are going to answer the following question:

Which thickness, d , does an aluminum pipe with the area of $S = 1 \text{ m}^2$ have to have in order to ensure acceptable performance (probability of failure $P_f < 5\%$ at design service life, $t_s = 5$ years?)

Starting the Simulation

Use the data enter in the example above. **Change** the Calculation Type to **Fail Probability: Depth**

Under the **Calculation Parameters** grid, enter 1 m^2 for the **Surface Area** and 5 years for the **Service Life**. Change units by clicking on the **blue** hyperlinks.

Make sure all data sets are selected (checked)

Your screen should look like the image below.

OLI Studio - [EVS.oad]

File Edit Streams Calculations Chemistry Tools View Window Help

Navigator

- Document1
- EVS.oad
- Streams
 - EVS-Aluminum samples
 - EVS-Fail Probability

Actions

Plot Template Manager

Save

EVs EVS-Fail Probability

Description Definition Plot Report

Description	Pit Depth (µm)	Area (sq-m)
Calculation Parameters		
Surface Area		1.00000
Service Life (yr)		5.00000
Experiment Start (yr)	0	
Default Value		0.0129000
<input checked="" type="checkbox"/> One Week (yr)	0.0191781	
1	180.000	0.0129000
2	266.000	0.0129000
3	290.000	0.0129000
4	306.000	0.0129000
5	334.000	0.0129000
6	340.000	0.0129000
7	340.000	0.0129000
8	410.000	0.0129000
9	410.000	0.0129000
10	545.000	0.0129000
<input checked="" type="checkbox"/> One Month (yr)	0.0821918	
1	460.000	0.0129000
2	500.000	0.0129000
3	510.000	0.0129000
4	580.000	0.0129000
5	580.000	0.0129000
6	640.000	0.0129000
7	654.000	0.0129000
8	680.000	0.0129000
9	692.000	0.0129000
10	692.000	0.0129000

Add Group Elapsed Actual Time

Fail Probability: Depth Specs... Calculate

Summary

EVs Calculation Type: Failure Probability - Critical Depth Based

Calculation Parameter(s):
Surface Area 1.00000 sq-m
Service Life 5.00000 yr

Experiment Start: 01/01/2000

Range 0.0 to 2000.0 µm
Step size 10.0 µm
No. steps 200

Default Area Value: 129.000


For Help, press F1

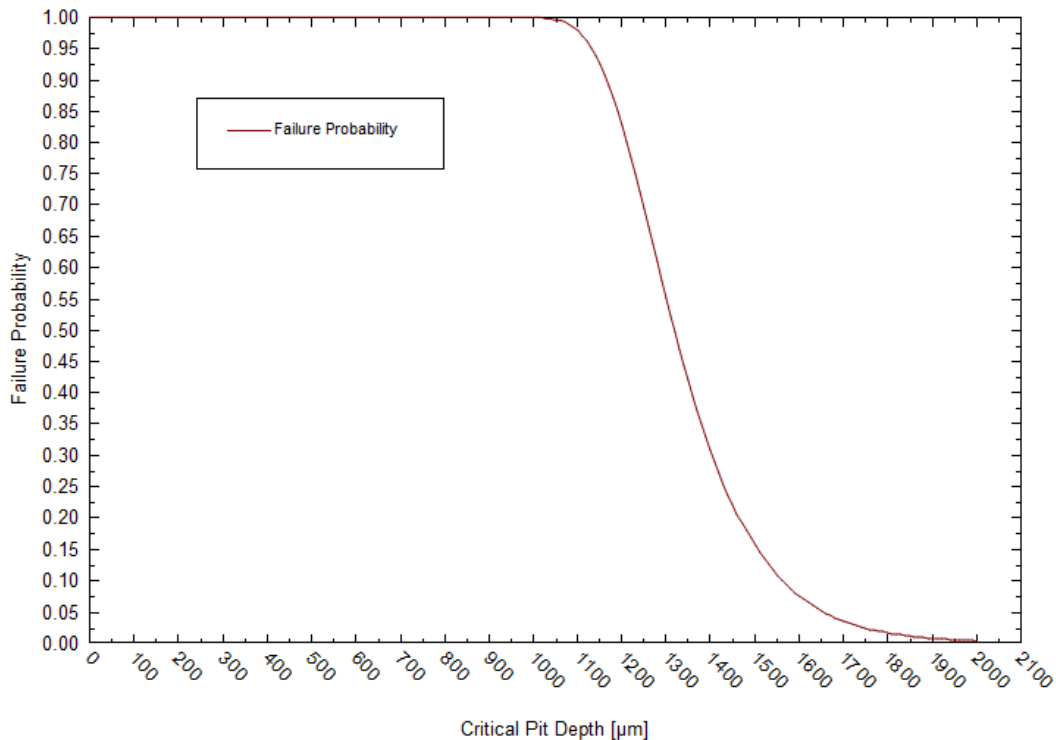
NUM

We are now 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.

Analyzing the results

Click on the **Plot** tab ( **Plot**). You will see a plot of predicted probability of failure



Click on the **Report** tab, and to the **Calculation Results** table.

We can conclude that the acceptable pipe wall width is reached at $d > 1950 \mu\text{m}$.

Fail Probability: Life

Let's continue with the calculation of Probability of failure for a given service time (life) and the area of the system as a function of penetration depth.

We are going to answer the following question:

What service life, t , will have the aluminum pipe with the width, $d=1850 \mu\text{m}$ with area $S=10 \text{ m}^2$ in order to ensure acceptable performance i.e. probability of failure, $P_f < 5 \%$?

Starting the Simulation

Change the Calculation Type to **Fail Probability: Life**

Under the **Calculation Parameters** grid, enter 10 m² for the **Surface Area** and 1850 μm for the **Critical Pit Depth**. Change units by clicking on the **blue** hyperlinks (If needed).

For this calculation we need to specify the period of time at which we want to bound the calculation.

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

Change the **Service Life** range as follows: Start=0 years, End=3 years and Increments=0.2 years. Then click **OK**.

EVS Calculation Options

Survey Range

Failure Probability - Service Life Based Unit: yr

Selected Range

0.0 to 3.0 in 15 steps of 0.2

New

Delete

Linear Log Point List

End Points

Start 0.0

End 3.00000

Step Size

Increment 0.200000 } Select one, the other is calculated

Number Steps 15

OK Cancel Apply Help

Your screen should look like the image below.


Description	Pit Depth (μm)	Area (sq-m)
Calculation Parameters		
Surface Area		10.0000
Critical Pit Depth	1850.00	
Experiment Start (yr)	0	
Default Value		0.0129000
<input checked="" type="checkbox"/> One Week (yr)	0.0191781	
1	180.000	0.0129000
2	266.000	0.0129000
3	290.000	0.0129000
4	306.000	0.0129000
5	334.000	0.0129000
6	340.000	0.0129000
7	340.000	0.0129000
8	410.000	0.0129000
9	410.000	0.0129000
10	545.000	0.0129000
<input checked="" type="checkbox"/> One Month (yr)	0.0821918	
1	460.000	0.0129000
2	500.000	0.0129000
3	510.000	0.0129000
4	580.000	0.0129000
5	580.000	0.0129000
6	640.000	0.0129000
7	654.000	0.0129000
8	680.000	0.0129000
9	692.000	0.0129000

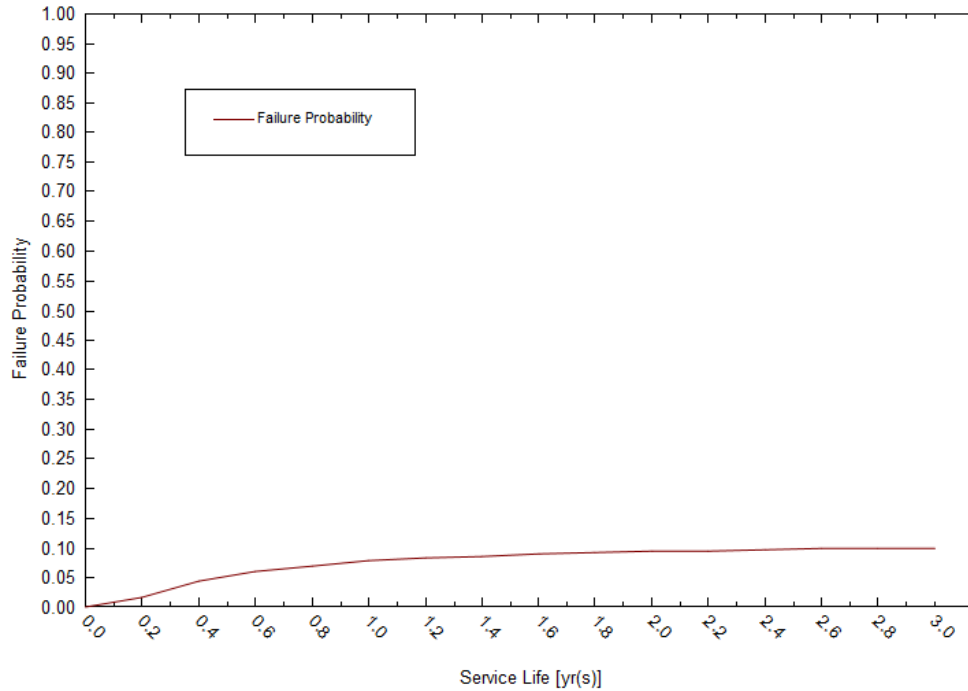
Add Group Elapsed Actual Time

We are now 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.

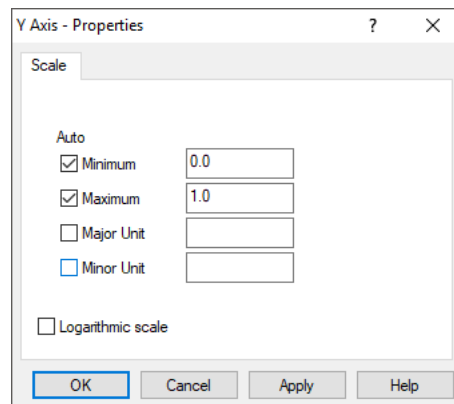
Analyzing the results

Click on the **Plot** tab ( **Plot**). You will see a plot of predicted probability of failure. We need to modify the plot to see the results in more detail.

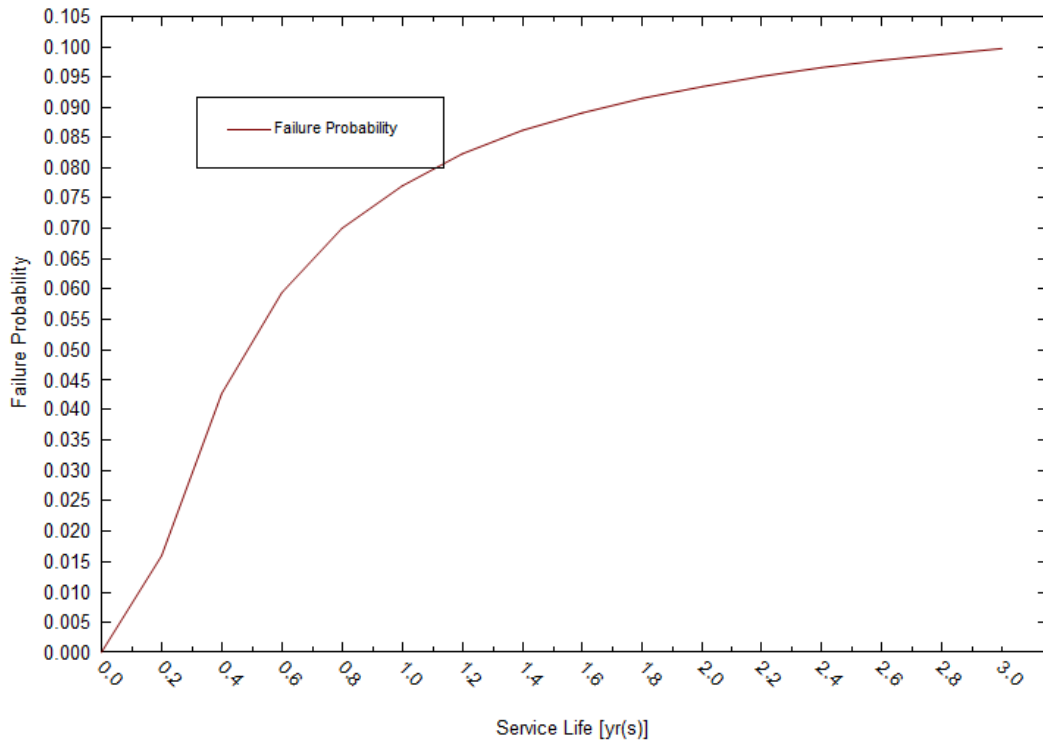


Double click on the **Y axis**. This will open a new window.

Check the boxes **Minimum** and **Maximum**. Then click **OK**.



The plot should look like the image below



The maximum probability of failure seems to be at around 10%.

Click on the **Report** tab, and to the **Calculation Results** table.

We can conclude that the lifetime of this pipe before failing is <0.6 years.

Fail Probability: Area

Finally, let's do the calculation of Probability of failure for a given penetration depth and service time as a function of the area of the system.

We are going to answer the following question:

What area, S , can have the aluminum pipe with the width, $d=2000 \mu\text{m}$ and service life $t=5$ years in order to ensure acceptable performance i.e. probability of failure, $P_f < 5\%$?

Starting the Simulation

Change the Calculation Type to **Fail Probability: Area**

Under the **Calculation Parameters** grid, enter $2000 \mu\text{m}$ for **Critical Pit Depth** and 5 years for the **Service Life**. Change units by clicking on the **blue** hyperlinks (If needed).

For this calculation we need to specify the surface area range that we want to survey.

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

Change the **Surface Area** range as follows: Start=0 sq-m, End=100 sq-m and Number of steps=50. Then click **OK**.

EVS Calculation Options

Survey Range

Failure Probability - Surface Area Based Unit: sq-m

Selected Range

0.0 to 100.0 in 50 steps of 2.0

New

Delete

Linear Log Point List

End Points

Start 0.0

End 100.000

Step Size

Increment 2.00000 } Select one, the other is calculated

Number Steps 50

OK Cancel Apply Help

Your screen should look like the image below.

Description Definition Plot Report


Description	Pit Depth (µm)	Area (sq-m)
Calculation Parameters		
Critical Pit Depth	2000.00	
Service Life (yr)		5.00000
Experiment Start (yr)	0	
Default Value		0.0129000
One Week (yr)	0.0191781	
1	180.000	0.0129000
2	266.000	0.0129000
3	290.000	0.0129000
4	306.000	0.0129000
5	334.000	0.0129000
6	340.000	0.0129000
7	340.000	0.0129000
8	410.000	0.0129000
9	410.000	0.0129000
10	545.000	0.0129000
One Month (yr)	0.0821918	
1	460.000	0.0129000
2	500.000	0.0129000
3	510.000	0.0129000
4	580.000	0.0129000
5	580.000	0.0129000
6	640.000	0.0129000
7	654.000	0.0129000
8	680.000	0.0129000
9	692.000	0.0129000

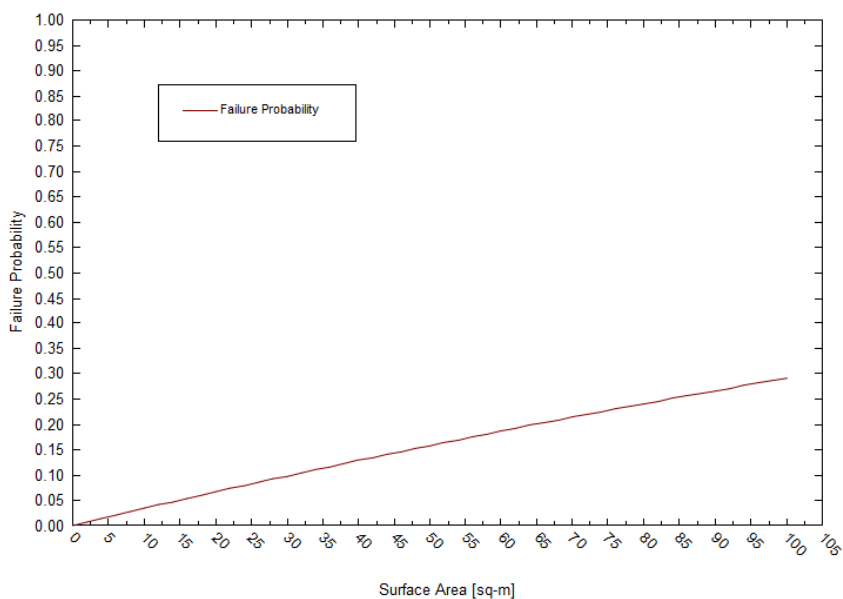
Add Group Elapsed Actual Time

We are now 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.

Analyzing the results

Click on the **Plot** tab ( **Plot**). You will see a plot of predicted probability of failure. We need to modify the plot to see the results in more detail.



The maximum probability of failure seems to be at around 30%.

Click on the **Report** tab, and to the **Calculation Results** table.

We can conclude that acceptable performance is reached at $<14 \text{ m}^2$.

Example 58: Failure Analysis due to Corrosion in Pipelines

In this example, we will show how in some cases reliable prediction of corrosion damage can be done by using a very limited number of experimental points.

In the table below, you can see the results of direct measurements of the depth of the deepest pits in the pipeline between Samara and Moscow [Zikerman, 1972].

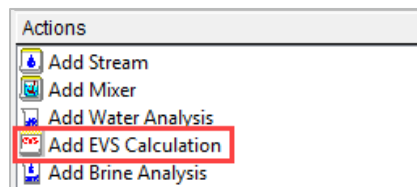
Pit depths (mm) for pipeline between Samara and Moscow

	Group 1	Group 2	Group 3	Group 4	Group 5	Group 6	Group 7	Group 8
Sample	1440 h	5040 h	5760 h	8959 h	12624 h	17688 h	28032 h	28272 h
1	0.1			1.4	1.7	1.9		2.1
2		0.49		1.95	2.1	2.08		2.25
3	0.3	1.6		1.8				
4	0.4			1.6	1.65	1.88		
5	0.9		1.57	2.1	2.21	2.4	2.4	
6	0.3		1.2	1.4	1.4	1.55	1.71	

Calculation the Depth of the Deepest Pit

Starting the Simulation

Add a new **EVS** calculation. Select the **Add EVS Calculation** icon in the Actions Pane



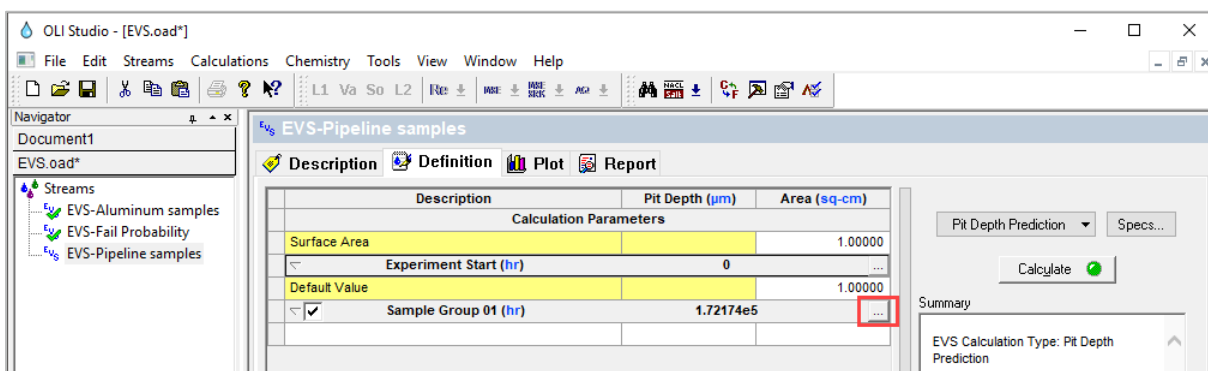
Click on the new EVS calculation and press **<F2>** to change the name to *EVS-Pipeline samples*. Notice that the default calculation is the *Pit Depth Prediction*.

Under the **Calculation Parameters** grid, enter 1 cm² for the **Surface Area** and **Default Value** cells.

Note: Because the area of the pipelines metal was not changed with time the information about this area is not needed for extrapolation of corrosion damage in time.

Since the data is in hours, click on the blue hyperlink **day** and change it to hours (**hr**) (for both: The **Experiment Start** and the **Sample Group**).

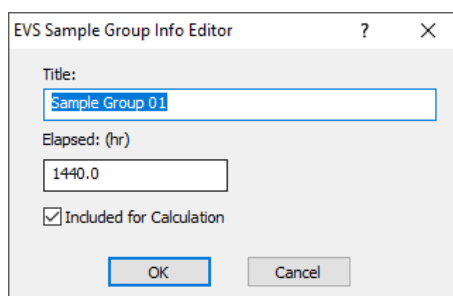
Your screen should look like the image below:



There are experimental data sets for 8 different periods of time. This means that we need to enter 8 different sample groups.

By default, **Sample group 01** is created. Click on the button to edit this field. This will open a new window.

Leave the default name as **Sample Group 01**, enter the number **1440** for the number of **elapsed hours**, and **check** the box **'Include for Calculation'**



Enter the **Pit Depth** data (second column) obtained for 1440 hours.

Description	Pit Depth (mm)	Area (sq-cm)
Calculation Parameters		
Surface Area		1.00000
Experiment Start (hr)	0	...
Default Value		1.00000
<input checked="" type="checkbox"/> Sample Group 01 (hr)	1440.0	...
1	0.100000	1.00000
3	0.300000	1.00000
4	0.400000	1.00000
5	0.900000	1.00000
6	0.300000	1.00000

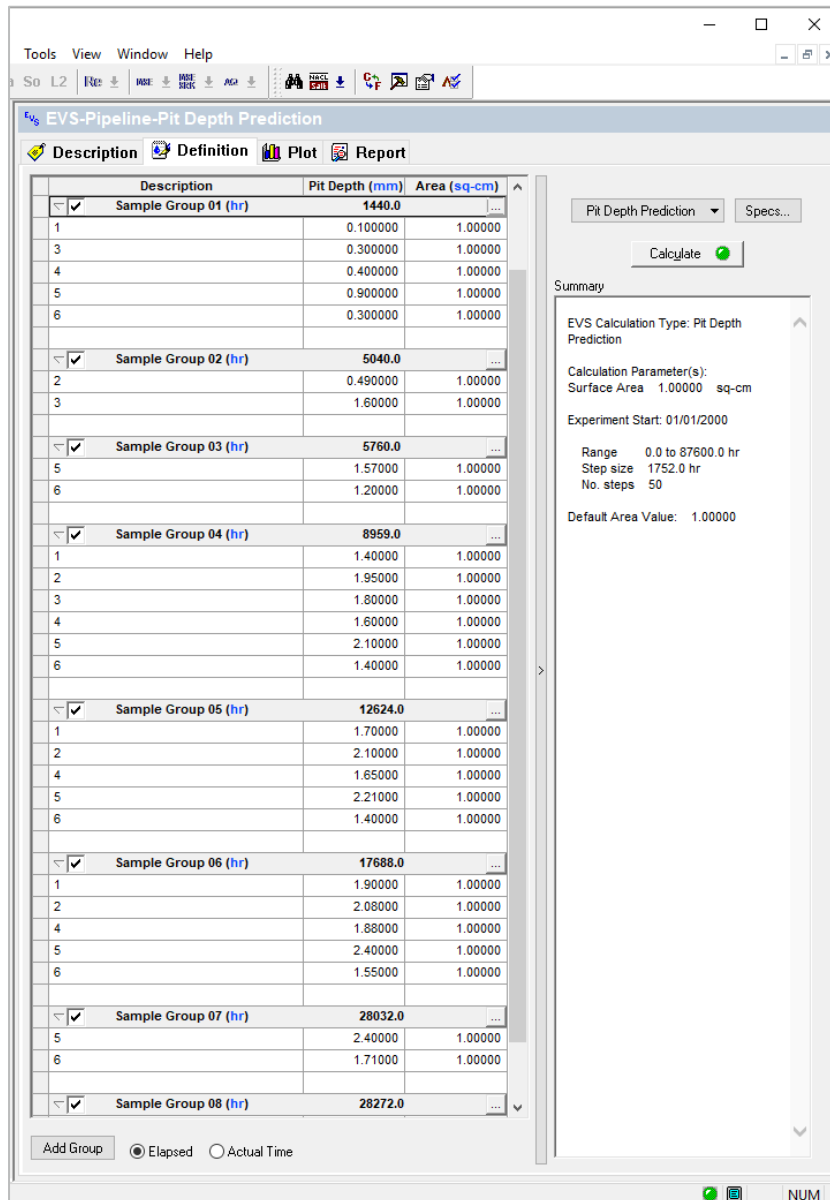
Now we need to add 7 more groups.

Click on the **Add Group** button (located at the bottom of the window. This will open a new window.

Leave the default name as **Sample Group 02**, enter the number 5040 for the number of **elapsed hours**, and **check** the box **'Include for Calculation'**. Then click **OK**.

Enter the **Pit Depth** data (second column) obtained for 5040 hours. Click on the **Add Group** button, and repeat the same procedure for 5760, 8959, 12624, 17688, 28032 and 28272 hours.

Once you have entered all the experimental data, your screen should look like the image below.

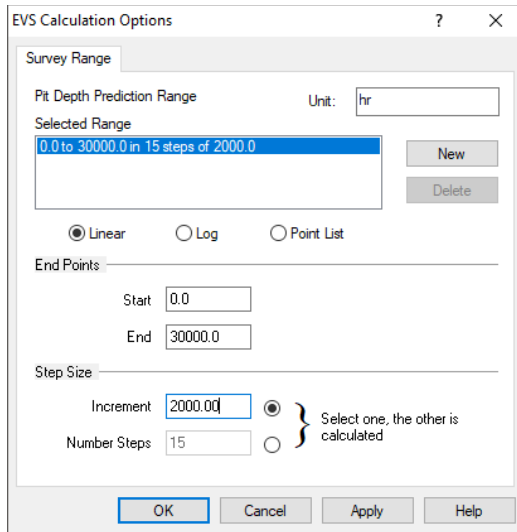


Make sure that all the groups are selected (checked) to be considered for the calculation.

At this point, the experimental data has been entered. Now we need define the period of time for which we want to do the prediction of failure due to pitting.

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

Under the **Survey Range** tab, enter the range for **Pit Depth Prediction** as follows: Start=0 hours, End=30000 hours, and Increment=2000 hours. Then click **OK**



Before running the calculation, we are going to study two different cases:
 The first case will include the experimental data from groups 01 to 05
 The second case will include all the experimental data from groups 01 to 08


Calculation including Groups 01 to 05

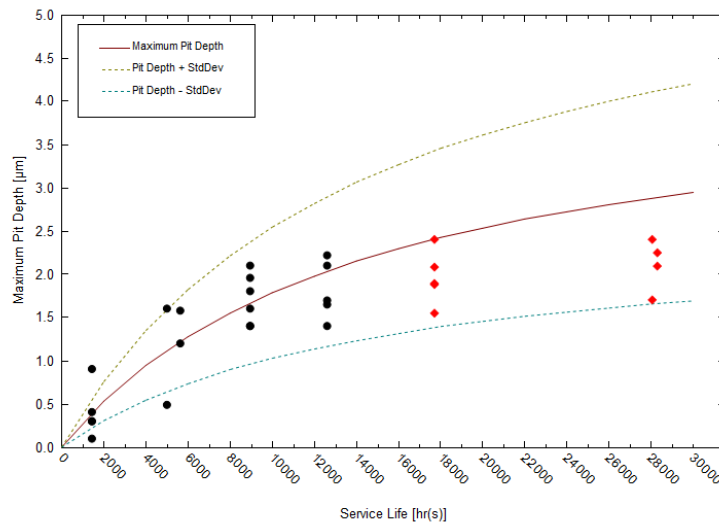
Check the boxes for Group 01 to 05

We are now 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. Save it under the same file that we previously created as *EVS calculations*.

Analyzing the results

Click on the **Plot** tab ( **Plot**). You will see a plot of the predicted mean value of the depth of the deepest pit, x_m and the plots of values $x_m - \sigma$ and $x_m + \sigma$, where σ is the standard deviation of x_m .



As previously noted, only the points in black mean that were used for predicting propagation of corrosion damage. The red diamonds mean that were not taken into account for the calculation and are shown only for demonstrating the accuracy of prediction.

Calculation including Groups 01 to 08

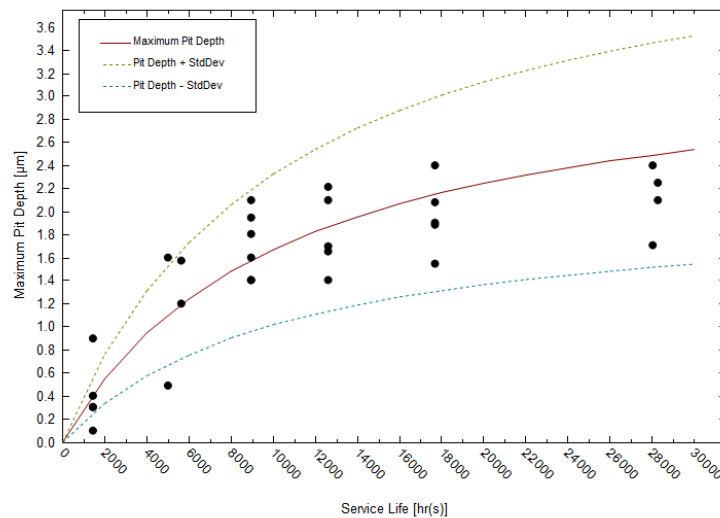
Check the boxes for Group 01 to 08

We are now 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. Save it under the same file that we previously created as *EVS calculations*.

Analyzing the results

Click on the **Plot** tab ( **Plot**).



The plot above show how the predicted results improved with increasing number of subsequent inspections.

Note: The predictions can be substantially improved if they were obtained on the same part of the pipe where conditions are approximately the same.

Click on the **Report** tab, and to the **Calculation Results** table.

You can see here that at 30,000 hours the maximum pit depth predicted is $1.55 \mu\text{m} \leq 2.54 \mu\text{m} \leq 3.53 \mu\text{m}$.

Example 59: Predicting the Pit Depth with Insufficient Data

In some cases, the data that provided by the user may be insufficient for reliable prediction of corrosion damage. The table below, shows experimental data (obtained from Laycock et al. 1990) for depths of the deepest pits that were measured on 316L coupons (2 x 2 x 1/2 in) in a 10% ferric chloride solution at 50 °C.

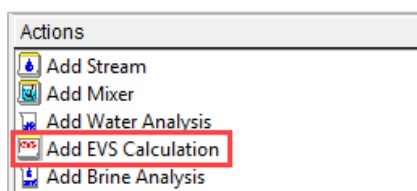
Pit Depth Data for an area of $s = 25.8 \text{ cm}^2$, depth in μm

Sample	Grp 1	Grp 2	Grp3	Grp 4	Grp 5	Grp 6	Grp 7	Grp 8	Grp 9
	40.5 h	144.17 h	215.33 h	292.5 h	331.0 h	378.5 h	453.25 h	477.0 h	528.0 h
1	775	1326	1036	912	1361	1613	2101	1722	1714
2		1176	1199	1173	1534	1641	2024	1798	1767
3								1496	1775

Calculation the Depth of the Deepest Pit

Starting the Simulation

Add a new **EVS** calculation. Select the **Add EVS Calculation** icon in the Actions Pane

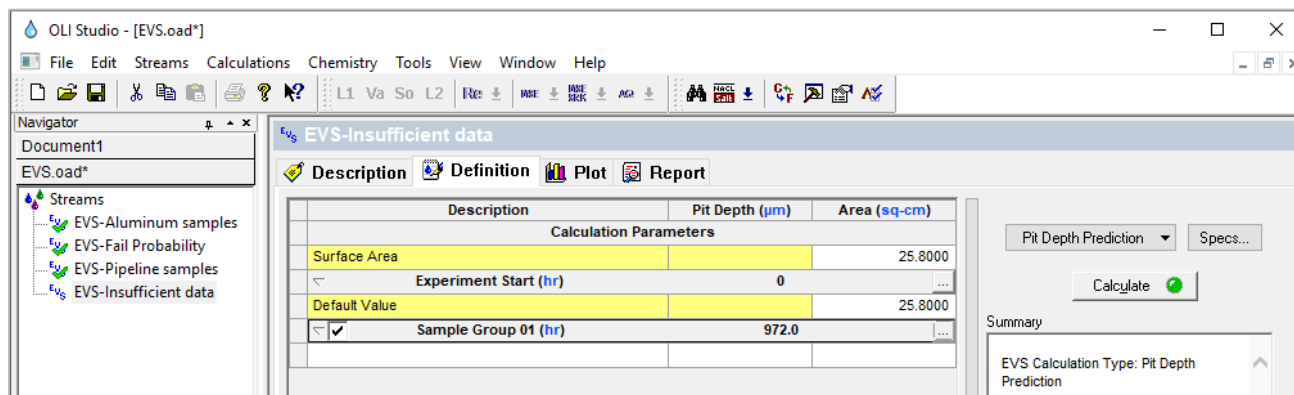


Click on the new EVS calculation and press <F2> to change the name to *EVS-Insufficient Data*. Notice that the default calculation is the *Pit Depth Prediction*.


Under the **Calculation Parameters** grid, enter 25.8 cm² for the **Surface Area** and **Default Value** cells.

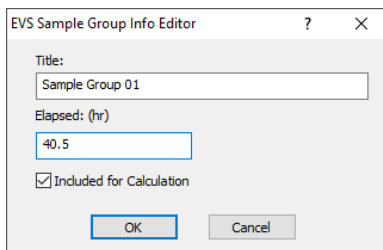
Since the data is in hours, click on the blue hyperlink **day** and change it to hours (**hr**) (for both: The **Experiment Start** and the **Sample Group**).

Your screen should look like the image below:



There are experimental data sets for 9 different periods of time. This means that we need to enter 9 different sample groups.

By default, **Sample group 01** is created. Click on the  button to edit this field. This will open a new window. **Leave** the default name as **Sample Group 01**, enter the number **40.5** for the number of **elapsed hours**, and **check** the box **'Include for Calculation'**



Enter the **Pit Depth** data (second column) obtained for 40.5 hours.

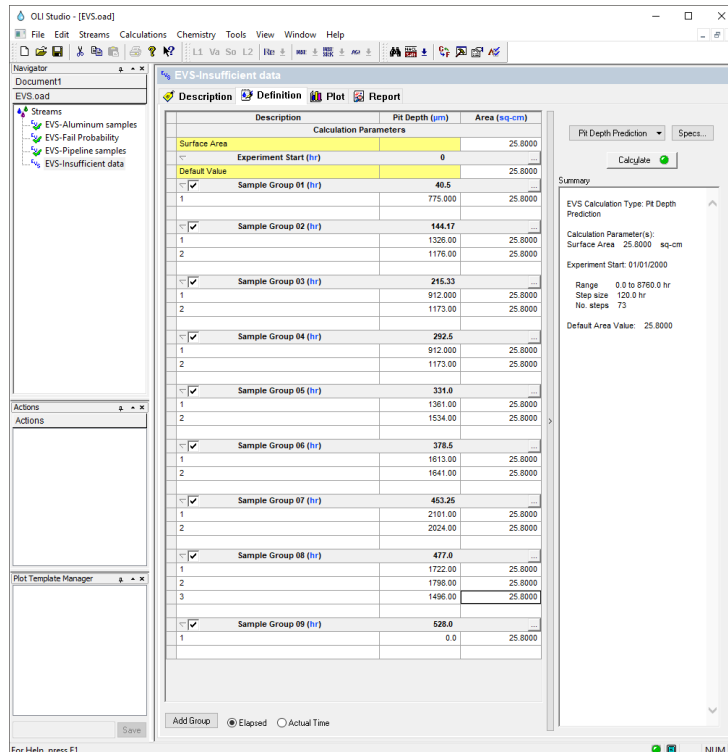
Now we need to add 8 more groups.

Click on the **Add Group** button (located at the bottom of the window. This will open a new window. **Leave** the default name as **Sample Group 02**, enter the number 144.17 for the number of **elapsed hours**, and **check** the box **'Include for Calculation'**. Then click **OK**.

Enter the **Pit Depth** data (second column) obtained for 144.17 hours.

Click on the **Add Group** button, and repeat the same procedure for the rest of the experimental data (groups)

Once you have entered all the experimental data, your screen should look like the image below.



At this point, the experimental data has been entered. Now we need define the period of time for which we want to do the prediction of failure due to pitting.

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

Under the **Survey Range** tab, enter the range for **Pit Depth Prediction** as follows: Start=0 hours, End=580 hours, and number of steps=50 hours. Then click **OK**

The screenshot shows the 'EVS Calculation Options' dialog box with the 'Survey Range' tab selected. The 'Pit Depth Prediction Range' section has a 'Unit' of 'hr'. The 'Selected Range' list contains one entry: '0.0 to 580.0 in 50 steps of 11.6'. Below this are radio buttons for 'Linear' (selected), 'Log', and 'Point List'. The 'End Points' section has 'Start' set to 0.0 and 'End' set to 580.000. The 'Step Size' section has 'Increment' set to 11.6000 and 'Number Steps' set to 50. A note indicates that either 'Increment' or 'Number Steps' can be selected, but only one is calculated. At the bottom are 'OK', 'Cancel', 'Apply', and 'Help' buttons.

Before running the calculation, we are going to study two different cases:

The first case will include the experimental data from groups 01 to 03
The second case will include all the experimental data from groups 01 to 09

Calculation including Groups 01 to 03

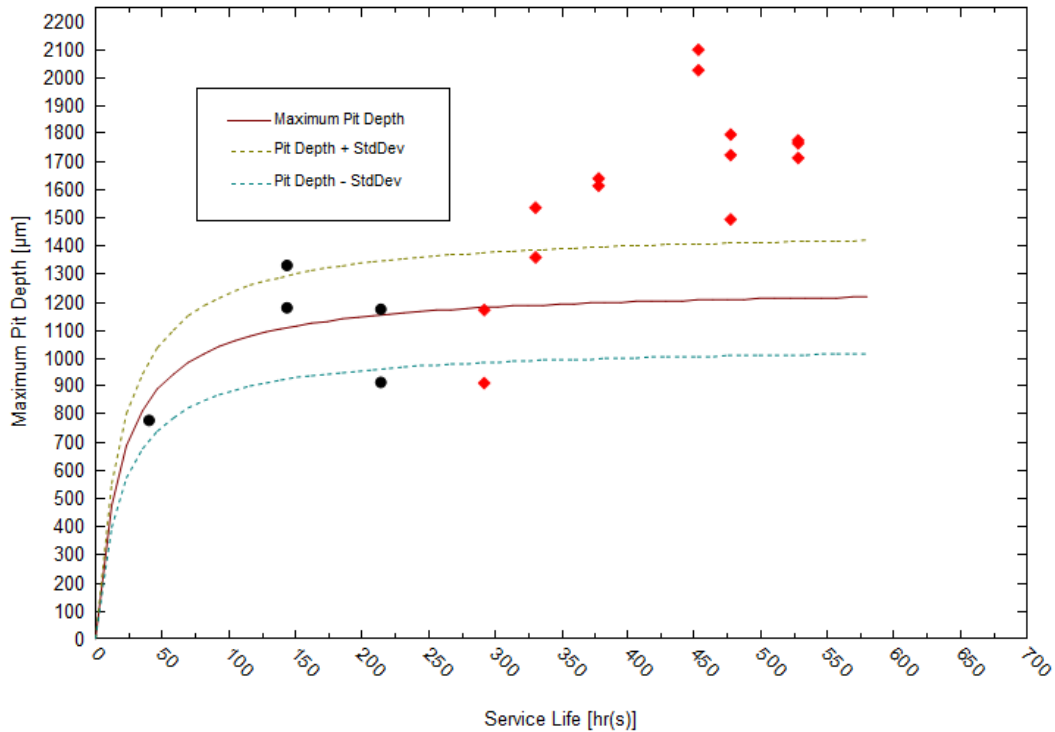
Check the boxes for Group 01 to 03

We are now 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. Save it under the same file that we previously created as *EVS calculations*.

Analyzing the results

Click on the **Plot** tab ( **Plot**).



We see that in this case the prediction cannot be considered satisfactory. The reason is that for the first, second, and third observation times the observed mean value of deepest pit decreases. Obviously, such behavior of maximum pit depth has no physical foundation. Generally speaking, such situation is the result of an insufficient numbers of experiments (used coupons) for given observation times. Accordingly, we can expect that after increasing the number of used coupons the situation can improve.

Calculation including Groups 01 to 09

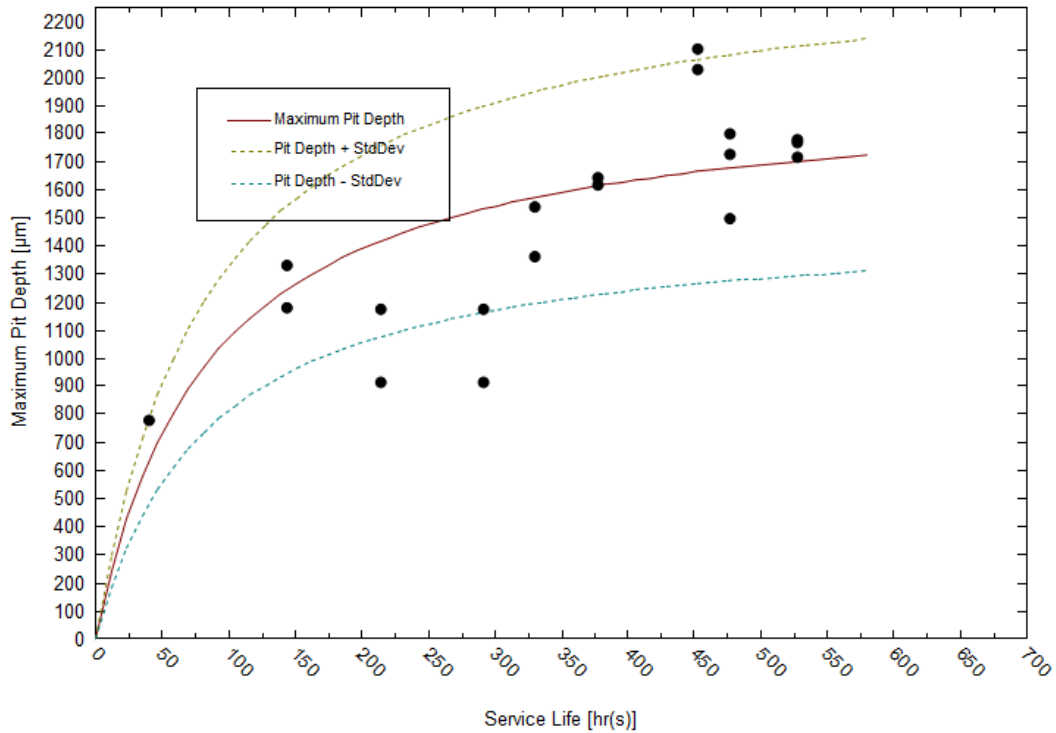
Check the boxes for Group 01 to 09

We are now 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. Save it under the same file that we previously created as *EVS calculations*.

Analyzing the results

Click on the **Plot** tab ( Plot).



The plot above show how the predicted results improved with increasing number of subsequent inspections.

The plot above also shows that the results of approximation of the full set of available experimental data from Laycock et al. 1990) can be reasonably approximated by using EVS approach.

Additionally, these results show that insufficient number of coupons (measurements at given observation times) can be compensated by increasing numbers of observation at different times.

Click on the **Report** tab, and to the **Calculation Results** table.

You can see here that at 580 hours the maximum pit depth predicted is $1309.93 \mu\text{m} \leq 1724.09 \mu\text{m} \leq 1724.09 \mu\text{m}$.

Chapter V – OLI Studio: ScaleChem

think simulation | getting the chemistry right is a module within the OLI Studio. A separate license enables this module.

Why Use OLI Studio: ScaleChem?

Scale problems arise when fluid, initially in equilibrium with its environment, is disturbed and becomes unstable. The unstable fluid results in H₂O, CO₂, and H₂S partitioning across the water, oil, and gas phases, corrosion of metal surfaces, and precipitation/dissolution of solids. think simulation | getting the chemistry right recognizes all three effects, which are all important to the oil and gas production professional.

Precipitates form when mineral-forming elements increase the concentration of produced waters beyond supersaturation, or the saturation point. The primary causes of supersaturation are pressure, temperature, phase partitioning, and fluid mixing. think simulation | getting the chemistry right quantifies the effects on mineral scale potential while calculating the physical and chemical properties of fluid and gas phases. Industry professionals can use the software's calculations to help determine the best methods to deal with scaling situations.

think simulation | getting the chemistry right can be used to calculate scaling at one or more user specified temperatures and pressures. Other calculation options include the ability to mix waters at user specified ratios to find compatible waters, and the ability to saturate a water with respect to one or more solids to simulate reservoir conditions.

There are different types of inputs and calculation objects that can be used in think simulation | getting the chemistry right. A brief definition of each type of calculation is given below.

Input Objects

There are three different types of input objects, also referred to as analysis types, in the think simulation | getting the chemistry right software: Brine Analysis, Oil Analysis and Gas Analysis.



Add Brine
Analysis

think simulation | getting the chemistry right refers to all waters and aqueous samples as brines. This option is added by double clicking on the **Add Brine Analysis**. A brine can be a surface water, an injection water, a formation water, a production water or any other type of aqueous fluid you can create. Brine compositions are entered in terms of ionic concentrations. In addition, the brine pH, total inorganic carbon and alkalinity can also be specified.



Add Oil
Analysis

Add Oil Analysis allows you to enter an oil (non-aqueous phase). The oil sample may consist of pure component hydrocarbons (e.g., alkanes), distillation data, pseudocomponents or all three.



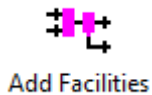
Add Gas Analysis allows you to enter any hydrocarbon mixture which may or may not contain water, carbon dioxide or hydrogen sulfide. The default hydrocarbon is methane (CH_4) but the hydrocarbon list may be expanded to include higher carbon numbers.

Calculation Objects

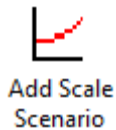
There are five different types of calculations that can be carried out in think simulation | getting the chemistry right: Saturator, Facilities, Scale Scenario, Scale Contour, and Mixing Water. A brief definition of each type of calculation is given below.



Add Saturator object combines fluids at the specified temperature and pressure and saturates the combined phases with the selected minerals.



Add Facilities mixes and separates fluids. It is used to simulate production operations.



Add Scale Scenario object calculates the scaling of minerals from a fluid as temperature and pressure changes, e.g. at different production locations..



Add Scale Contour object calculates the scaling of minerals from a fluid over a matrix of temperature and pressure. It creates a 2D contour plot visual.



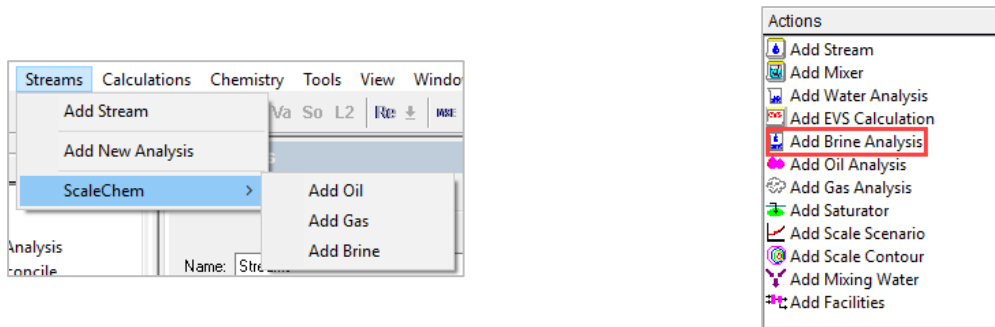
Add Mixing Water object mixes two potentially incompatible brines together to identify at what ratios the scale will form.

In this chapter we will model a hypothetical field and learn how to use and set up each one of the objects presented above.

Section 11. Entering a Brine Analysis in think simulation | getting the chemistry right

Entering Data for a Brine Analysis

To add a **Brine Analysis**, go to the toolbar menu and click on **Streams > ScaleChem > Add Brine**, or by selecting the **Add Brine Analysis** icon in the Actions Pane.



You will see three different tabs for this analysis. The **Description**, **Design** and **Report** tab.

The Brine Analysis open in the **Design**, which has 2 different sub-tabs: **Data Entry** and **Reconcile**, where we need to enter the laboratory analysis information.

✓ Description
🔍 Design
📄 Report

Data Entry

Reconcile

Variable	Value	Balanced
Cations (mg/L)		
Na+1	0.0	0.0
K+1	0.0	0.0
Ca+2	0.0	0.0
Mg+2	0.0	0.0
Sr+2	0.0	0.0
Ba+2	0.0	0.0
Fe+2	0.0	0.0
Anions (mg/L)		
Cl-1	0.0	0.0
SO4-2	0.0	0.0
HCO3-1	0.0	0.0
HS-1	0.0	0.0
C2H3O2-1	0.0	0.0
Neutrals (mg/L)		
CO2	0.0	0.0
H2S	0.0	0.0
SiO2	0.0	0.0
B(OH)3	0.0	0.0

Entry Options

Units
mg/L

Display
Formula

Show Non-zero Only
 Show Balanced Column

Template Manager
Standard
Save as...

Balance Options
Type
Dominant Ion

We will start in the **Data Entry** (red) sub-tab. Here you enter the concentration of Cations, Anions, and Neutrals. This sub-tab comes already prepopulated with some of the most common cations, anions, and neutrals species found in laboratory water/brine analyses (by default the units are in **mg/L**). If your species is not present in the prepopulated grid, simply click on the white grid and type the ion or neutral of interest. If it is a **cation**, type the element followed by a plus (+) sign and the corresponding oxidation state, e.g., Cu+2. If it is an **anion**, type the element followed by a minus (-) sign and the corresponding oxidation state, e.g., Br-1. If it is a **neutral**, simply type the species either using the formula name or its chemical name, as has been shown in the previous sections.

The Brine Analysis grid also contains search aids to find a specific cation, anion, or neutral species. The first search aid is the drop list located in each the cation, anion, and neutral grid sections. The list is alphabetic and is activated using the drop-down arrow within the cell, after the first few letters of the ion is typed.

Description Design Report

Data Entry

Variable	Value	Balanced
Cations (mg/L)		
Na+1	0.0	0.0
K+1	0.0	0.0
Ca+2	0.0	0.0
Mg+2	0.0	0.0
Sr+2	0.0	0.0
Ba+2	0.0	0.0
Fe+2	0.0	0.0
Cu		
CO2	0.0	0.0
H2S	0.0	0.0
SiO2	0.0	0.0
B(OH)3	0.0	0.0

Reconcile

Display Name	OLI Name
↕ Cs+1	CSION
OLI CSION	CSION
SYN Cu(+)	CUIION
SYN Cu(++)	CUION
SYN Cu(+1)	CUIION
SYN Cu(+2)	CUIION

Entry Options

Units: mg/L

Display: Formula

Show Non-zero Only

Show Balanced Column

Template Manager

Standard

Save as...

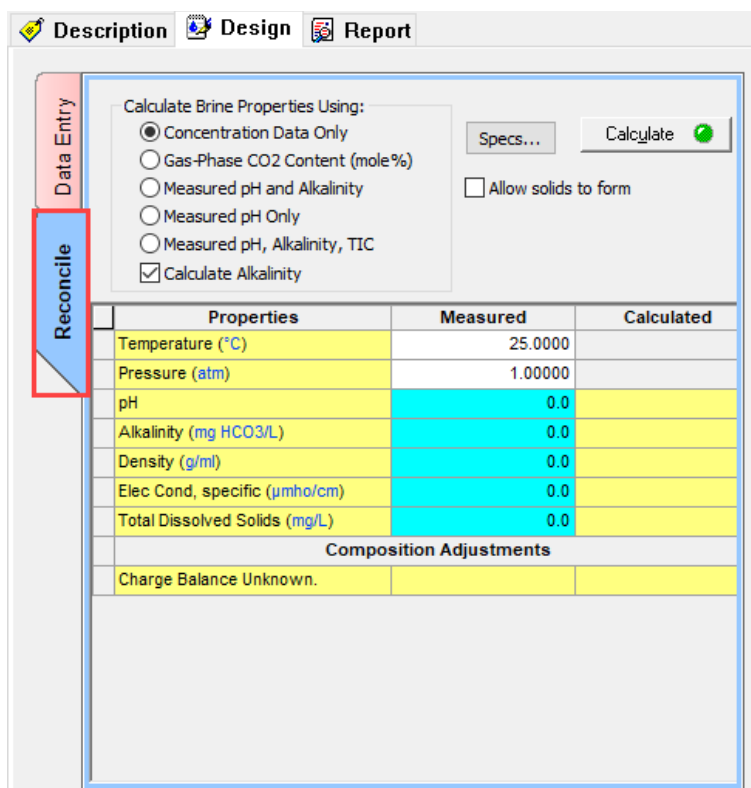
Balance Options

Type: Dominant Ion

If a name is misspelled or if the text is unrecognized, then a red 'X' appears to the left of the name. This name needs to be corrected or the row deleted before proceeding. To delete the row, simply select the wrong entry (which will turn black) and hit the key **<Delete>**.

Neutrals (mg/L)		
CO2	0.0	0.0
H2S	0.0	0.0
SiO2	0.0	0.0
B(OH)3	0.0	0.0
X oli	0.0	0.0

The **Reconcile** sub-tab is used to define the measured properties of the brine. In this **Reconcile** sub-tab, we will tell the software how to reconcile the brine.



The first step, however, is to enter the brine measured properties and conditions. To do this we need to start in the **Properties | Measured | Calculated** table.

Properties	Measured	Calculated
Temperature (°C)	25.0000	
Pressure (atm)	1.00000	
pH	0.0	
Alkalinity (mg HCO ₃ /L)	0.0	
Density (g/ml)	0.0	
Elec Cond, specific (µmho/cm)	0.0	
Total Dissolved Solids (mg/L)	0.0	
Composition Adjustments		
Charge Balance Unknown.		

By default, the values of temperature, and pressure are 25°C and 1 atm. The **aqua-blue** cells indicate the values that you need to enter if they were measured at the temperature and pressure specified, these are: Measured pH, Measured Alkalinity¹⁰, Density, Specific Electrical Conductivity and Total Dissolved Solids (TDS).

You can always change the units of these properties by clicking on the units highlighted in **blue**. This action will open the Units Manager Window.

If you don't have a measured property value, for example, the Specific Electrical Conductivity, just leave it blank.

¹⁰ This is generally a reliable value, unless solids have precipitated in the sample. Alkalinity is often but not always the same value as the bicarbonate ion (HCO₃⁻). ScaleChem Analyzer can reconcile on a measured alkalinity by adjusting the solution composition.

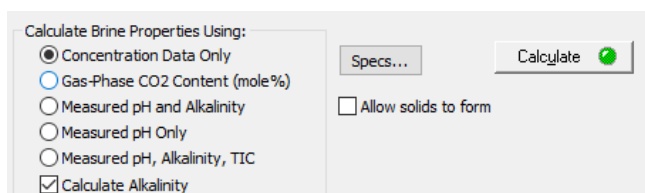
The yellow cells, under the **Calculated** column, will contain calculated values by the software and will be shown once the simulation is run.

When reviewing laboratory analysis of brine samples, it is quite common for the positive ions (cations) and the negatively charged ions (anions) in solution to not balance. This may be due to the precision limits of the various experimental procedures used to measure the ions - i.e. some ions may not have been analyzed. These solutions must have a neutral charge. think simulation | getting the chemistry right will adjust/modify inflows in order to balance the charges and make the solution neutral. This adjusting procedure is referred to as **Reconciliation**.

There are 5 different types of **Reconciliation Options**:

- Concentration Data Only
- Gas-phase CO2 content (mole%)
- Measured pH and Alkalinity
- Measured pH Only
- Measured pH, Alkalinity, TIC

Additionally, there is the option to calculate the alkalinity value by checking the **Calculate Alkalinity** box.



When the Reconciliation Option is selected, the software will calculate the properties of the brine

A more detailed description of each reconciliation option is given in Section 11.3. Reconciliation Options in the Brine Analysis below.

Brine Analyses - Reporting Elements

Brine analysis data obtained from ICP measurements will contain concentrations for B, P, S, and Si. These elements do not exist in the water, rather they exist as dissolved ions. If they are part of your analysis, then you should convert them to the following before entering them into the Brine Analyses object.

Converting element concentration to species for Brine Analysis

	Aqueous Species	Formula to enter	Formula weight multiplier
B, boron	Boric Acid	H3BO3	B (mg/l) × 5.72 = H3BO3 (mg/l)
Si, Silicon	Silica	SiO2	Si (mg/l) × 2.14 = SiO2 (mg/l)
P, Phosphorus	Dihydrogen Phosphate	H2PO4-1	P (mg/l) × 3.13 = H2PO4 (mg/l)
S, Sulfur	Sulfate or Sulfide	HS-1 or SO4-2 (cannot tell from total S only)	S (mg/l) × 1.03 for HS-1 (mg/l) or S (mg/l) × 3.0 for SO4-2 (mg/l)

Reconciliation Options in the Brine Analysis - Definitions

When reconciling a Brine Analysis, there are five options for reconciliation:

Concentration Data Only: The software will run an electroneutrality reconciliation only, and then compute the water properties such as pH, density, etc., based on the entered concentration of neutral, cations, and anions species. In the **Concentration Data Only** option you may allow the program to pick the species to adjust for electroneutrality or you may manually choose the species to perform the adjustment. ([See electroneutrality options](#)).

Gas-phase CO₂ content (mole%): Frequently it is simpler and more stable to measure the gas-phase CO₂ that is separated from the brine at the sampling point. When matched with another measured variable, usually alkalinity, the concentration of the carbonate species and the pH can be calculated. think simulation | getting the chemistry right performs a CO₂ gas fraction calculation by taking the P_{CO2} and the calculated alkalinity (based on the water analysis data) to reconcile the system for pH and carbonate properties. The CO₂ is adjusted to match a saturated gas composition.

Measured pH Only: Many brines analyses report a measured pH. This pH may or may not match the pH calculated by the software. The cause may be an incomplete and/or inaccurate brine description. The software will run both an electroneutrality and pH reconciliation. This type of reconciliation will match your recorded pH. Additionally, the software will compute the water properties such as, density, electrical conductivity, etc. The pH of the solution is automatically adjusted by the software by adding either HCl or NaOH, or you may select your preferred acids and bases to adjust the pH.

Measured pH and Alkalinity: The purpose of the Measured pH and Alkalinity reconciliations is to match the computed pH and alkalinity values with those you measured. The software will run an electroneutrality, pH and alkalinity reconciliation. Additionally, the software will compute the water properties such as density, electrical conductivity, etc. The pH of the solution is automatically adjusted by the software by adding either HCl or NaOH or you may select your preferred acids and bases to adjust the pH. The Alkalinity is automatically calculated by the software, using CO₂ as the alkalinity titrant, H₂SO₄ as the alkalinity pH titrant and 4.5 as the alkalinity end point pH. You can also change to a different alkalinity titrant if you prefer.

Measured pH, Alkalinity, TIC: The purpose of this reconciliation is to match the measured pH, total alkalinity, and the total inorganic carbon (TIC). The Total Inorganic Carbon (TIC) is adjusted using CO₂ as the alkalinity titrant, H₂SO₄ as the alkalinity pH titrant and 4.5 as the alkalinity end point pH. The software adjusts the acetate concentration (organic acids) to match the total Alkalinity value by adding or removing acetic acid. You cannot however change the CO₂ or acetic acid for the alkalinity adjustment. These are fixed by the software. The target pH is obtained simultaneously by HCl or NaOH. You may select your preferred acids and bases to adjust the pH instead of the default HCl and NaOH.

Additionally, there is the option to **Calculate Alkalinity**: Calculate Alkalinity . It is important to note, that this is only an alkalinity calculation based on the concentration entered, it is not an alkalinity reconciliation.

A Basic Brine Analysis

A brief introduction to the brine analysis tool will be shown in the example below. As we go through the example, the basic definitions, functionalities and reporting for the *Brine Analysis object* will be shown.

Example 60: Basic Brine Analysis

In this example, we will input dissolved species concentrations and other measured properties into a **Brine Analysis** object to model a hypothetical water sample. We will calculate the **pH** and **scaling tendency** of a brine sample based upon its measured composition at 1 atm and 25 °C.

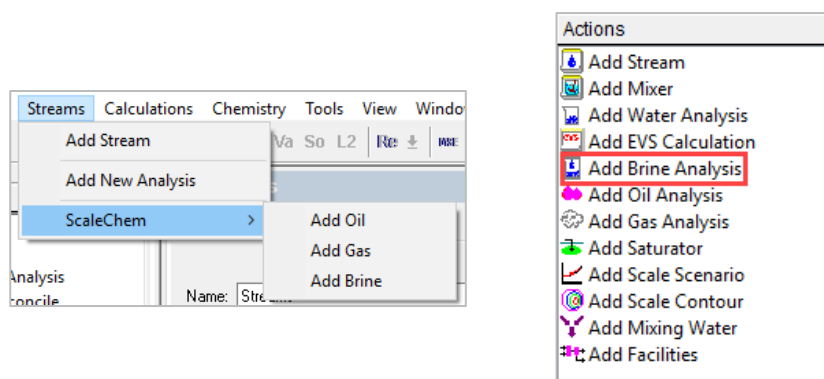
Starting the Simulation

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

Brine Analysis Composition							
Cations (mg/L)		Anions (mg/L)		Neutrals (mg/L)		Measured Properties	
Na+1	20400	Cl-1	37000	CO2	150	pH	7.1
K+1	400	SO4-2	2200	H2S	15	Alkalinity as HCO3-, mg/L	715
Ca+2	3800	HCO3-1	0				
Mg+2	830	HS-1	0				
Sr+2	15	C2H3O2-1	715				
Ba+2	0.7						
Fe+2	10						

Setting the Water Analysis

Add a **Brine Analysis**. Go to the toolbar menu and click on **Streams > ScaleChem > Add Brine**, or by selecting the **Add Brine Analysis** icon in the Actions Pane



Click on the new Brine and press **<F2>** to change the name to *Brine Analysis*
 Select the **AQ** thermodynamic Framework (remember that MSE is the default so please switch it)
Click on the **Names Manager** Icon and select the **Formula** option (default)
Click on the **Units Manager** Icon, and select Metric, Concentration (default)
 Under the **Design** Tab, enter the **Cation**, **Anion**, and **Neutrals** composition given in the table above.
 Your screen should look like the image below:

Variable	Value	Balanced
Cations (mg/L)		
Na+1	20400.0	20400.0
K+1	400.000	400.000
Ca+2	3800.00	3800.00
Mg+2	830.000	830.000
Sr+2	15.0000	15.0000
Ba+2	0.700000	0.700000
Fe+2	10.0000	10.0000
Anions (mg/L)		
Cl-1	37000.0	38938.1
SO4-2	2200.00	2200.00
HCO3-1	0.0	0.0
HS-1	0.0	0.0
C2H3O2-1	715.000	715.000
Neutrals (mg/L)		
CO2	150.000	150.000
H2S	15.0000	15.0000
SiO2	0.0	0.0
B(OH)3	0.0	0.0

Note: It is highly unusual for the data to be electrically neutral. Therefore, the software reconciles the sample for **electroneutrality**. After entering each species concentrations, you will notice that the software shows a yellow column named **Balanced**. The software balances charges according to the selected ion option and displays this in the yellow column.

There are 4 different Balance Options:

- 1) **Dominant Ion:** This is the default method. The largest concentration ion is used to adjust the electroneutrality. In our example, 1938.077 mg/L of Cl-1 are added since there is an excess of positive charge (see the above image).
- 2) **Prorate Cations:** All cations are adjusted up or down equally
- 3) **Prorate Anions:** All anions are adjusted up or down equally
- 4) **Make-up Ion:** This option allows for a single ion species to be adjusted. User selects an ion to increase or decrease.

Select **Dominant Ion** as balance option
Click on the **Reconcile** (vertical blue tab)

Notice that the five different types of reconciliations are available in in the upper left corner of the window (see image below). Also, you can see the **Calculate Alkalinity** box (Calculate Alkalinity) option, which allows you to compute the alkalinity, based on the concentration entered.

Select the Concentration Data Only option. This option means that the software will compute the water properties based on the current concentration of neutral, cation, and anion species. The calculation will not use the measured pH, or the measured alkalinity entered (if any).

Enter the **measured properties:** pH = 7.1 and Alkalinity = 715 as mg HCO3/L

Description Design Report File Viewer

Data Entry

Reconcile

Calculate Brine Properties Using:

Concentration Data Only
 Gas-Phase CO2 Content (mole%)
 Measured pH and Alkalinity
 Measured pH Only
 Measured pH, Alkalinity, TIC
 Calculate Alkalinity

Allow solids to form

Properties	Measured	Calculated
Temperature (°C)	25.0000	
Pressure (atm)	1.00000	
pH	7.10000	
Alkalinity (mg HCO3/L)	715.000	
Density (g/ml)	0.0	
Elec Cond, specific (µmho/cm)	0.0	
Total Dissolved Solids (mg/L)	0.0	
Composition Adjustments		
Add Charge Balance (mg/L Cl-1)		

Summary

Unit Set: [Metric \(mass concentration\)](#)

Automatic Chemistry Model
[Aqueous \(H+ ion\) Databanks:](#)
[Aqueous \(H+ ion\)](#)
 No Solid phase(s)
 Using K-fit Polynomials
 T-span: 25.0 - 225.0
 P-span: 1.0 - 1500.0

Stream Parameters:

Temperature (°C)	25.0000
Pressure (atm)	1.00000
Stream amount (L)	1.00000

Dominant Ion Charge Balance (eq/L):

Cation Charge	1.15621
Anion Charge	-1.10155
Imbalance	0.0546661

Ion(s) needed to balance (mg/L):

Cl-1	1938.077
------	----------

Concentration Data Only.

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: *ScaleChem Analysis Calculations*.

Analyzing the Results

Once the calculation is done, the **Calculated** column displays the results obtained based on the concentrations entered in the **Data Entry** tab. Notice that the calculated results are pH=5.31 and Alkalinity=263.0 mg HCO₃⁻/L vs the measured values of pH=7.1 and Alkalinity=715 mg HCO₃⁻/L.

Calculate Brine Properties Using:

- Concentration Data Only
- Gas-Phase CO₂ Content (mole%)
- Measured pH and Alkalinity
- Measured pH Only
- Measured pH, Alkalinity, TIC
- Calculate Alkalinity

Specs... Calculate

Allow solids to form

Properties	Measured	Calculated
Temperature (°C)	25.0000	
Pressure (atm)	1.00000	
pH	7.10000	5.31413
Alkalinity (mg HCO ₃ /L)	715.000	263.001
Density (g/ml)	0.0	1.04487
Elec Cond, specific (µmho/cm)	0.0	91637.7
Total Dissolved Solids (mg/L)	0.0	67370.0
Composition Adjustments		
Add Charge Balance (mg/L Cl-1)		1938.08

Summary

Unit Set: Metric (mass concentration)

Automatic Chemistry Model
Aqueous (H+ ion) Databanks:
Aqueous (H+ ion)
No Solid phase(s)
Using K-fit Polynomials
T-span: 25.0 - 225.0
P-span: 1.0 - 1500.0

Stream Parameters:

Temperature (°C)	25.0000
Pressure (atm)	1.00000
Stream amount (L)	1.00000

Dominant Ion Charge Balance (eq/L):

Cation Charge	1.15621
Anion Charge	-1.10155
Imbalance	0.0546661

Ion(s) needed to balance (mg/L):

Cl-1 1938.077

Concentration Data Only.

Phase Amounts:

Aqueous (g) 1044.87

Aqueous Phase Properties:

pH	5.31413
Ionic Strength (mol/mol)	0.0226409
Density (g/ml)	1.04487

Calc. elapsed time: 9.227 sec.
Calculation complete
The brine is supersaturated with 2

To the right you can see the results summarized in the **Summary Box**.

The top section contains the **Stream Parameters** information. In this example, the software performed the calculation at 25 °C, 1 atm, and a total Stream amount of 1 L.

The **Dominant Ion Charge Balance** section shows the type of balance that was used to reach electroneutrality, which cation/anion was deficient, and how much of it was added.

The **Phase amounts** section shows the distribution of species in the different phases. This analysis contains two phases: aqueous and vapor.

The **Aqueous Phase Properties** information shows the computed pH, ionic strength, and density of the solution. It is important to note here that the measured pH is 7.1 and the computed pH is 5.31. The density of this solution is 1.04487 g/ml. Remember, for this example the software used only the concentration of neutrals, cations, and anions in solution to do a reconciliation.

Click on the **Report** tab and scroll down to the **Pre and Post Scaling Tendencies** table.

Pre and Post Scaling Tendencies

Scale Mineral	Pre-scaling	Pre-index	Post-scaling	Post-index
BaSO4 (Barite)	9.41306	0.973731	9.41306	0.973731
CaCO3 (Calcite)	0.0252328	-1.59803	0.0252328	-1.59803
CaSO4.2H2O (Gypsum)	0.936931	-0.0282926	0.936931	-0.0282926
CaSO4 (Anhydrite)	0.738602	-0.131590	0.738602	-0.131590
FeCO3 (Siderite)	2.71223e-3	-2.56667	2.71223e-3	-2.56667
FeS (Pyrrhotite)	16.3375	1.21319	16.3375	1.21319
KCl (Sylvite)	6.72353e-4	-3.17240	6.72353e-4	-3.17240
FeS (Mackinawite)	0.278931	-0.554504	0.278931	-0.554504
NaCl (Halite)	0.0122286	-1.91262	0.0122286	-1.91262
SrCO3 (Strontianite)	2.96599e-4	-3.52783	2.96599e-4	-3.52783
SrSO4 (Celestine)	0.200644	-0.697574	0.200644	-0.697574

From this table, you can see that Barite and Pyrrhotite solids have been predicted to be supersaturated.

For more detailed information about scaling tendencies, you can go to Scaling section on page 179.

Scroll down to the **Brine Composition** table

Brine Composition

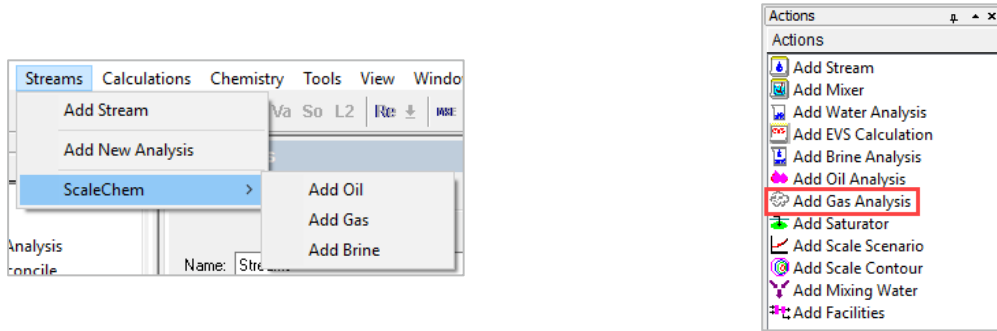
Cations	Value (mg/L)	Anions	Value (mg/L)	Neutrals	Value (mg/L)
K(+1)	400.000	Cl(-1)	38938.1	CO2	107.419
Na(+1)	20400.0	HCO3- (*)	59.0364	H2S	15.0000
Ba(+2)	0.700000	SO4-2	2200.00		
Ca(+2)	3800.00	Acetate-	545.141		
Fe(+2)	10.0000				
Mg(+2)	830.000				
Sr(+2)	15.0000				

This table shows the composition of the brine after the reconciliation (calculation) has taken place.

Section 12. Entering a Gas Analysis in think simulation | getting the chemistry right

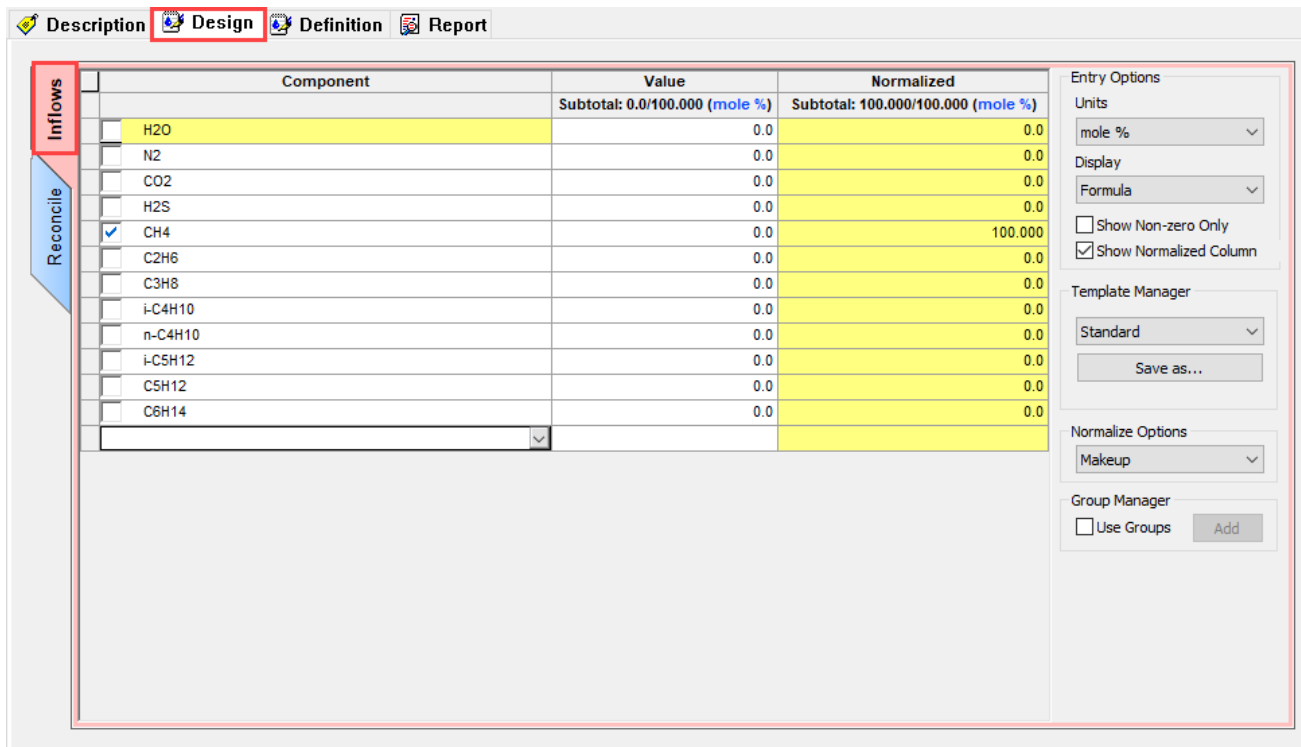
Entering Data for a Gas Analysis

To add a **Gas Analysis**, go to the toolbar menu and click on **Streams > ScaleChem > Add Gas**, or by selecting the **Add Gas Analysis** icon in the Actions Pane.



You will see four different tabs for this analysis. The **Description**, **Design**, **Definition** and **Report** tab.

The gas analysis opens in the **Design** tab, which has 2 different sub-tabs: **Inflows** and **Reconcile**, where we need to enter the laboratory gas analysis information.



We will start in the **Inflows** (red) sub-tab. Here you enter the concentration of a pure-component hydrocarbon gas, in **mole %** units. The standard list of component extents to C6 alkanes.

If there is a component that is not present in the prepopulated grid, simply click on the white grid and type the species of interest, using the formula name or its chemical name, as has been shown in the previous sections. Let's say for example, you want to add Isooctane. Type isooctane or i-C8H18 in the white cell to add it to the list.

There is also the option of using the drop-down arrow, that allows you to search for the specific components you want to add.

The screenshot shows the 'Inflows' table with columns for Component, Value, and Normalized. A dropdown menu is open for the 'i-C8H18' entry, listing various chemical species. The 'i-C8H18' entry is highlighted in blue. The table also shows a 'Reconcile' button on the left and 'Entry Options' on the right.

Component	Value	Normalized
H2O	0.0	0.0
CH4	0.0	100.000
N2	0.0	0.0
CO2	0.0	0.0
H2S	0.0	0.0
C2H6	0.0	0.0
C3H8	0.0	0.0
i-C4H10	0.0	0.0
n-C4H10	0.0	0.0
i-C5H12	0.0	0.0
C5H12	0.0	0.0
C6H14	0.0	0.0
i-C8H18	0.0	0.0

Drop-down menu items:

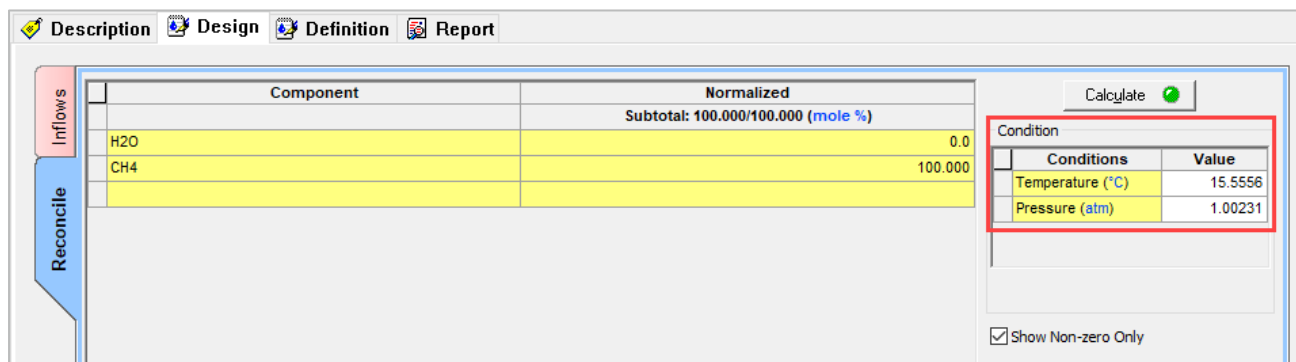
Display Name	OLI Name
i-C4H10	ISOBUTANE
i-C5H12	IPENTAN
i-C8H18	MEPNTAN224
I2	IOD2EL
SYN BA	IBUTYLAMN
OLI IRFN7FNF	IRFN7FNF

If a name is misspelled or if the text is unrecognized, then a red 'X' appears to the left of the name. This name needs to be corrected or the row deleted before proceeding. To delete the row, simply select the wrong entry (which will turn black) and hit the key **<Delete>**.

The screenshot shows the 'Inflows' table with the 'OLI' entry highlighted in black and a red 'X' next to it. The table also shows a 'Reconcile' button on the left and 'Entry Options' on the right.

Component	Value	Normalized
H2O	0.0	0.0
CH4	0.0	100.000
N2	0.0	0.0
CO2	0.0	0.0
H2S	0.0	0.0
C2H6	0.0	0.0
C3H8	0.0	0.0
i-C4H10	0.0	0.0
n-C4H10	0.0	0.0
i-C5H12	0.0	0.0
C5H12	0.0	0.0
C6H14	0.0	0.0
i-C8H18	0.0	0.0
OLI	0.0	0.0

The **Reconcile** sub-tab is used to calculate the properties of the gas at the temperature and pressure conditions specified. By default, the values of temperature, and pressure are 60 °F (15.56°C) and 14.7 psia (1.002 atm).



A Basic Gas Analysis

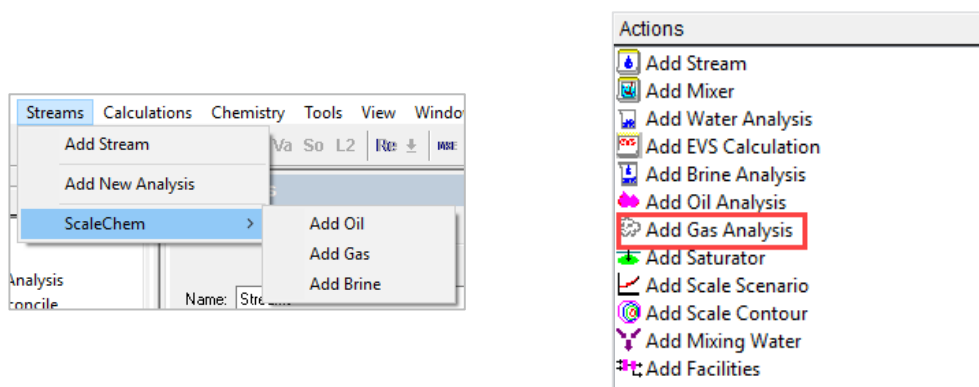
A brief introduction to the gas analysis tool will be shown in the example below. As we go through the example, the basic definitions, functionalities, and reporting for the *Gas Analysis object* will be shown.

Example 61: Basic Gas Analysis

The Gas Analysis object provides a quick way to enter a pure-component hydrocarbon gas.

Setting the Gas Analysis

Add a Gas Analysis. Go to the toolbar menu and click on **Streams > ScaleChem > Add Gas**, or by selecting the **Add Gas Analysis** icon in the Actions Pane



Click on the new Gas Analysis and press **<F2>** to change the name to *Gas Analysis*

Select the **AQ** thermodynamic Framework (Remember that MSE is the default so you need to change it)

Click on the **Names Manager** Icon and select the **Formula** option (default)

Click on the **Units Manager** Icon, and select Metric, Mole Frac. (default)

Under the **Inflows** Tab, enter the gas composition given in the table below

Gas Analysis Composition		
Formula	Component Name	Mole %
H2O	Water	1.80
N2	Nitrogen	3.00
CO2	Carbon Dioxide	1.50
H2S	Hydrogen Sulfide	0.50
CH4	Methane	65.5
C2H6	Ethane	14.0
C3H8	Propane	8.00
i-C4H10	Isobutane	1.00
n-C4H10	n-Butane	3.00
i-C5H12	Isopentane	0.50
C5H12	n-Pentane	0.70
C6H14	n-Hexane	0.50

Your screen should look like the image below:

The screenshot shows a software interface with a menu bar (Description, Design, Definition, Report) and a main window. On the left, there are two vertical tabs: 'Inflows' (top, red) and 'Reconcile' (bottom, blue). The 'Reconcile' tab is active, displaying a table with the following data:

Component	Value	Normalized
Subtotal: 100.000/100.000 (mole %)		Subtotal: 100.000/100.000 (mole %)
H2O	1.80000	1.80000
N2	3.00000	3.00000
CO2	1.50000	1.50000
H2S	0.500000	0.500000
CH4	65.5000	65.5000
C2H6	14.0000	14.0000
C3H8	8.00000	8.00000
i-C4H10	1.00000	1.00000
n-C4H10	3.00000	3.00000
i-C5H12	0.500000	0.500000
C5H12	0.700000	0.700000
C6H14	0.500000	0.500000

On the right side of the interface, there are several control panels:

- Entry Options:** Units (mole %), Display (Formula), Show Non-zero Only, Show Normalized Column.
- Template Manager:** Standard, Save as...
- Normalize Options:** Makeup.
- Group Manager:** Use Groups, Add.

Note: There are several options to the right of the data entered.

Entry options: Here you can select the preferred units, and display name. You also have the option to show the non-zero values only – sometimes the composition of species is zero – and also show the normalized (yellow) column – this option is useful when the values don't add up to 100 mole%.

Template manager: Here you can select the standard (default) template or the extended template – which includes hydrocarbons with longer chains. You can also create and save your own template for future use.

Normalize options: When your analysis does not add up 100 mole% you can select between two options: Make-up and Prorate. For the Make-up option, the default gas used is CH4.

Click on **Reconcile** (vertical blue tab). The reconciliation calculation will be calculated at 15.556 C and 1.00231 atm (standard conditions).

Component	Normalized	Reconciled Gas
	Subtotal: 100.000/100.000 (mole %)	Subtotal: 100.000/100.000 (mole %)
H2O	1.80000	1.75645
N2	3.00000	3.00133
CO2	1.50000	1.50066
H2S	0.500000	0.500221
CH4	65.5000	65.5290
C2H6	14.0000	14.0062
C3H8	8.00000	8.00355
i-C4H10	1.00000	1.00044
n-C4H10	3.00000	3.00133
i-C5H12	0.500000	0.500222
CSH12	0.700000	0.700310
CBH14	0.500000	0.500222

Conditions	Value
Temperature (°C)	15.5556
Pressure (atm)	1.00231

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: *ScaleChem Analysis Calculations*.

Analyzing the Results

Once the calculation is done, the **Reconciled Gas** column displays the results at equilibrium conditions.

Component	Normalized	Reconciled Gas
	Subtotal: 100.000/100.000 (mole %)	Subtotal: 100.000/100.000 (mole %)
H2O	1.80000	1.75645
N2	3.00000	3.00133
CO2	1.50000	1.50066
H2S	0.500000	0.500221
CH4	65.5000	65.5290
C2H6	14.0000	14.0062
C3H8	8.00000	8.00355
i-C4H10	1.00000	1.00044
n-C4H10	3.00000	3.00133
i-C5H12	0.500000	0.500222
CSH12	0.700000	0.700310
CBH14	0.500000	0.500222

Summary

Unit Set: Metric (mole fraction)

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

Stream Parameters:
Temperature (°C) 15.5556
Pressure (atm) 1.00231

Makeup Normalization: CH4.

Equilibrium Calculation.

Phase Amounts:
Aqueous (mol) 0.0443282
Vapor (mol) 99.9557
Solid (mol) 0.0
2nd Liquid (mol) 0.0

Aqueous Phase Properties:
pH 4.75177
Ionic Strength (mol/mol) 3.20592e-7
Density (g/ml) 0.999257

Calc. elapsed time: 0.940 sec.
Calculation complete

To the right you can see the results summarized in the **Summary Box**.

The top section contains the **Stream Parameters** information. In this example, the software performed an equilibrium calculation at 15.556°C and 1.00231 atm.

The **Phase amounts** section shows the distribution of species in the different phases. This analysis contains two phases: aqueous and vapor.

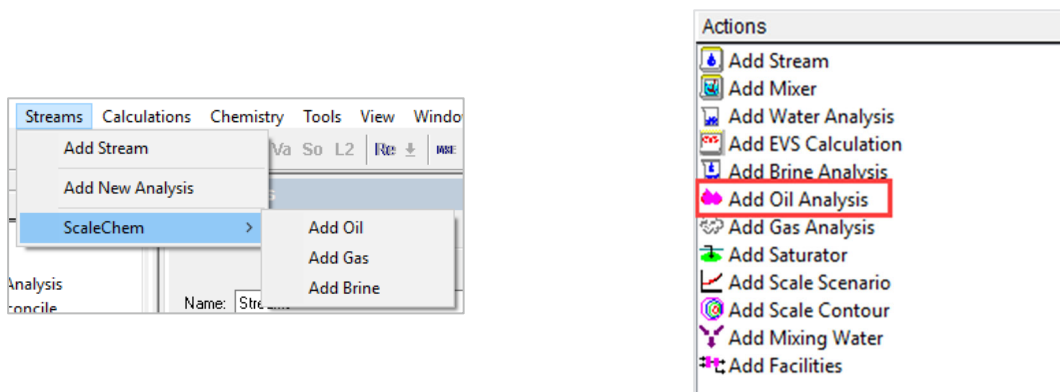
The **Aqueous Phase Properties** information shows the computed pH, ionic strength, and density of the solution.

Click on the **Report** tab. Here you will see a more complete representation of the results at equilibrium.

Section 13. Entering an Oil Analysis in think simulation | getting the chemistry right

Entering Data for an Oil Analysis

To add an **Oil Analysis**, go to the toolbar menu and click on **Streams > ScaleChem > Add Oil**, or by selecting the **Add Oil Analysis** icon in the Actions Pane.



You will see three different tabs for this analysis. The **Description**, **Design**, and **Report** tab.

The oil analysis opens in the **Design** tab, which has 4 different sub-tabs: **Combined**, **Pseudocomponents**, **Assay** and **Reconcile**.

In the **Combined** (red) sub-tab, pure components (organic and inorganic) are entered. If there is a component that is not present in the prepopulated grid, simply click on the white grid and type the species of interest, using the formula name or its chemical name, as has been shown in the previous sections. Let's say for example, you want to add Isooctane. Type isooctane or $i-C_8H_{18}$ in the white cell to add it to the list.

Also, you can use the **show non-zero only** option to hide all the zero values – since they are not needed.

Description Design Report

Component	Value	Normalized
n-C4H10	0.0	0.0
i-C5H12	0.0	0.0
C5H12	0.0	0.0
C6H14	0.0	0.0
C7H16	0.0	0.0
i-C8H18	0.0	0.0
n-C8H18	0.0	0.0
C9H20	0.0	0.0
C10H22	0.0	0.0
C11H24	0.0	0.0
C12H26	0.0	0.0
C13H28	0.0	0.0
C14H30	0.0	0.0
C15H32	0.0	0.0
C16H34	0.0	0.0
C17H36	0.0	0.0
C18H38	0.0	0.0
C19H40	0.0	0.0
C20H42	0.0	0.0
C21H44	0.0	0.0
C22H46	0.0	0.0
C23H48	0.0	0.0
C24H50	0.0	0.0
C25H52	0.0	0.0
C30H62	0.0	0.0
C35H72	0.0	0.0
C40H82	0.0	0.0

Entry Options
 Units: mole %
 Display: Formula
 Show Non-zero Only
 Show Normalized Column
 Template Manager: Standard

 Normalize Options: Prorate

In the **Pseudocomponents** (blue) sub-tab, you can enter pseudocomponents. Here you need to provide the molecular weight, NBP, SG, Thermodynamic Method, and the mole% information.

Component	Molecular Weight	Normal Boiling Point (°C)	Specific Gravity	Thermo Method	Value (mole %)
<Enter a name>					

In the **Assay** (red) sub-tab, distillation curves can be entered. The Assay screen contains three data entry grids: Component, Entry Options and Distillation Data.

Component Grid

Component	mole %
<Enter a name>	

Entry Options

Type: ASTM D86
 Thermo Method: API-8
 Density: 0.00
 Specific Gravity:
 No. of Cuts: 0

Distillation Data Grid

Volume%	Temperature (°C)

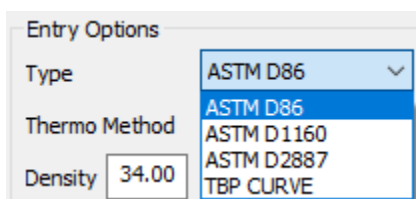
Assay Properties

Name	Mole %	Mol Wt.	NBP (°C)	Sp Gr	Cr Temp (°C)	Cr Pres (atm)	Cr Vol (L/mol)	Acentric Factor

Component Grid: In the component grid you can name your assay. No more than 5 letters are allowed for the name. The mole% instructs the software that the mole% entered represents the total hydrocarbon mass.

Entry Options Grid: In this grid there are four pieces of information that the user needs to fill out: The Assay Type, the Thermo Method, Density and No. of Cuts.

There are four Assay types. These are experimental methods used to create distillation curves.



Entry Options

Type	ASTM D86
Thermo Method	ASTM D1160
Density	34.00
No. of Cuts	

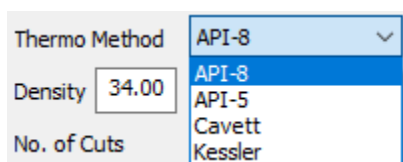
ASTM D86 runs at atmospheric pressures and is used for all oil types

ASTM D1160 runs at vacuum pressure and is used for heavy oils

ASTM D2887 runs on a gas chromatograph and is used for light oils

TBP is the true boiling point curve

There are also four methods for calculating thermodynamic properties, referred to as **Thermo Method** in the software, and these are: API-8, API-5, Cavett and Lee-Kessler.



Thermo Method

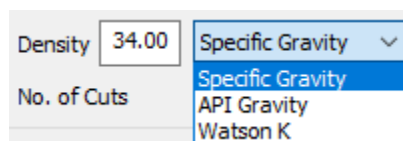
Density	34.00
No. of Cuts	

The **API-8** and **API-5** are methods that use specific gravity to determine critical parameters.

Cavett is a method to determine critical parameters using the API gravity

Lee-Kessler is a method to determine critical parameters by using the Watson K

There are three, average bulk density options: Specific Gravity, API gravity and Watson K.



Density

No. of Cuts	
-------------	--

Specific Gravity (SG) is the ratio of the material density to water. think simulation | getting the chemistry right requires specific gravity to be between 0.228 and 1.6.

API Gravity is defined as $API\ Gravity = (141.5/SG) - 131.5$

Watson K is a method that relates density to boiling point

A more detailed description of the different assay types, thermodynamic methods and density calculation methods is found in the Basic Definitions for the Oil Analysis Tool section on pages 393-396.

Distillation Data Grid: In this section the distillation data is entered.

The **Reconcile** tab is where the equilibrium calculations are performed and is used to calculate the properties of the gas at the temperature and pressure conditions specified. By default, the values of temperature, and pressure are 60 °F (15.556°C) and 14.7 psia (1.002 atm).

Component	Normalized
Subtotal: 100.000/100.000 (mole %)	
H2O	0.0
CH4	100.000

Conditions	Value
Temperature (°C)	15.5556
Pressure (atm)	1.00231

Basic Definitions for the Oil Analysis Tool

Hydrocarbon Petroleum Fractions

Frequently a hydrocarbon analysis is the only data available for entry into the software. This analysis is usually a distillation curve where the volume distilled as a function of temperature of a petroleum fraction has been analyzed. This information must be turned into a vapor, organic and aqueous component for use in the simulator.

ASTM D86

Used for light and medium petroleum products and is carried out at atmospheric pressure. The results are converted internally in the OLI model generator to a TBP (True Boiling Point Curve). This curve is then fit to a spline to smooth the curve. The cuts are taken from the spline.

ASTM D1160

Used for heavier petroleum products and is often carried out under vacuum. Sometimes as low as 1 mm Hg. The results are converted internally in the OLI model generator to a TBP (True Boiling Point Curve). This curve is then fit to a spline to smooth the curve. The cuts are taken from the spline.

ASTM D2887

Uses gas chromatography to produce the distillation curve and is applicable to a wide range of petroleum products. The results are always reported on a volume percent basis. The results are converted internally in the OLI model generator to a TBP (True Boiling Point Curve). This curve is then fit to a spline to smooth the curve. The cuts are taken from the spline

True Boiling Point (TBP)

These curves, in practice, are difficult to obtain. The other methods are usually used instead.

Thermodynamic Methods (pseudo-components and petroleum fractions)

The methods used within OLI to calculate the critical temperature and pressure are the API, Cavett and Lee-Kesler methods.

API Method

Uses the specific gravity to estimate the critical parameters. The specific gravity, if not entered, can be estimated from the API gravity or the Watson K. The boiling points are taken from the assay data. API version 5 (API-5) and API version 8 (API-8) are currently supported.

The API method is selected by the user. T_c , P_c , and V_c are calculated as follows:

$$T_c = 24.2787 \times T_b^{0.58848} \times SG^{0.3596}$$

$$\ln P_c = \frac{3.12281\rho + 9}{T_b^{2.3125} SG^{2.3201}} \text{ if } T_b < 1000 \text{ }^\circ\text{F}$$

Otherwise

$$\ln P_c = 8.3634 - \frac{0.566}{SG} - \left(0.24244 + \frac{2.2898}{SG}\right) + \left(\frac{0.11857}{SG^2}\right) \times 0.001 \times T_b$$
$$+ \left(1.4685 + \frac{3.648}{SG} + \frac{0.47127}{SG^2}\right) \times \left|\rho - 7 \times T_b^2 - \left(0.42019 + \frac{1.6977}{SG^2}\right)\right| \rho - 10 \times T_b^3$$

$$V_c = \frac{Z_c \times T_c \times 10.73}{P_c}$$

Where,

T_c = Critical temperature in Rankine

P_c = Critical pressure in psia

Z_c = Critical compressibility factor

$$Z_c = \frac{1}{3.43 + 6.7\rho - 9 \times \Delta^2}$$

And

$$\Delta = \frac{8.75 + 1.978(\log T_b) \times T_b}{1.8} \text{ if } T_c < 536.67 \text{ R}$$

If $536.67 < T_c < 593 \text{ R}$, the above result for Δ is multiplied by f:

$$f = \left(T_c - \frac{536.67}{T_c - T_b}\right)^{0.38}$$

If $T_c > 593 \text{ R}$,

$$\Delta = \left(\frac{(0.98907 \times SG)(\Delta - 592.4439)}{MW} \right)^{0.5}$$

Cavett

This method uses the API gravity method to determine the critical properties. The API gravity, if not entered can be estimated from the actual specific gravity or the Watson K. The boiling points for the pseudo-components are taken from the assay.

If the Cavett method is chosen by the user, T_c, P_c and V_c are calculated as follows:

$$T_c = 768.0712 + 1.7133693 \times T_b - 0.0010834 \times T_b^2 - 0.008921258 \times T_b \times API + (3.8890584\rho - 7) \\ + T_b^3 \times 5.309492\rho - 6 \times T_b^2 \times API + 3.27116\rho - 8 \times (T_b \times API)^2$$

$$\log P_c = 2.829046 + 0.0009412 \times T_b - 3.047475\rho - 5 \times T_b^2 - 2.087611\rho - 5 \times API \times T_b + 1.5184103\rho - 9 \times T_b^3 \\ + 1.1047809\rho - 8 \times API \times T_b^2 - 4.82716\rho - 8 \times API^2 \times T_b + 1.3949619\rho - 10 \times (API \times T_b)^2$$

$$V_c = \frac{Z_c \times T_c \times 10.73}{P_c}$$

Where,

T_c = Critical temperature in Rankine

P_c = Critical pressure in psia

Z_c = Critical compressibility factor

$$Z_c = \frac{1}{3.43 + 6.7\rho - 9 \times \Delta^2}$$

And

$$\Delta = \frac{8.75 + 1.978(\log T_b) \times T_b}{1.8} \text{ if } T_c < 536.67 \text{ R}$$

If 536.67 < T_c < 593 R, the above result for Δ is multiplied by f:

$$f = \left(T_c - \frac{536.67}{T_c - T_b} \right)^{0.38}$$

If T_c > 593 R,

$$\Delta = \left(\frac{(0.98907 \times SG)(\Delta - 592.4439)}{MW} \right)^{0.5}$$

Lee-Kesler

This method uses the Watson K and the specific gravity (which can be estimated via the Watson K) to determine the critical parameters.

If the Lee-Kesler method is selected by the user, T_c, P_c, and V_c are calculated as follows:

$$T_c = 341.7 + \frac{811}{SG} + (0.4244 + 0.1174 SG) \times T_b + (0.4669 - 3.2623 SG) + \frac{100,000}{T_b}$$

$$\ln P_c = 8.3634 - \frac{0.566}{SG} - \left(0.24244 + \frac{2.2898}{SG} + \frac{0.11857}{SG^2}\right) \times 0.001 \times T_b$$

$$+ \left(1.4685 + \frac{3.648}{SG} + \frac{0.47127}{SG^2}\right) \times \left|\rho - 7 \times T_b^2 - \left(0.42019 + \frac{1.6977}{SG^2}\right)\right| \rho - 10 \times T_b^3$$

$$V_c = \frac{Z_c \times T_c \times 10.73}{P_c}$$

Where,

Tc = Critical temperature in Rankine

Pc = Critical pressure in psia

Zc = Critical compressibility factor

$$Z_c = \frac{1}{3.43 + 6.7\rho - 9 \times \Delta^2}$$

And

$$\Delta = \frac{8.75 + 1.978(\log T_b) \times T_b}{1.8} \text{ if } T_c < 536.67 \text{ R}$$

If $536.67 < T_c < 593 \text{ R}$, the above result for Δ is multiplied by f:

$$f = \left(T_c - \frac{536.67}{T_c - T_b}\right)^{0.38}$$

If $T_c > 593 \text{ R}$,

$$\Delta = \left(\frac{(0.98907 \times SG)(\Delta - 592.4439)}{MW}\right)^{0.5}$$

Average Bulk Density

Specific Gravity

Unitless, relative to pure water (H₂O) at 15 °C which has a density of 1.0 g/mL

API Gravity

Degrees API (°API). This is calculated via the following equation:

$$API(60F) = \left(\frac{141.5}{s.g.(60F)}\right) - 131.5$$

where, SG is the specific gravity at 60 °F.

Watson K

The Watson K has no units but is calculated via:

$$K = \left(\frac{NBP^{1/3}}{SG} \right)$$

where NBP is the normal Boiling point.

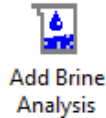
Putting together a complete calculation in think simulation | getting the chemistry right

Now that we have defined some terms, we are now ready to begin entering the information required to run a calculation. In this calculation we will be entering the concentrations of a single brine.

Task 1 – Create a Brine Analysis

In this task we will show the main interface of a Brine Analysis, followed by an example of a brine (water analysis) and calculate its scaling tendency. Steps for the simulation will be given with bullet points.

Add Brine Analysis from Actions Panel.



Click on the description Tab. If the **Description** tab is not currently displayed, click on the tab.



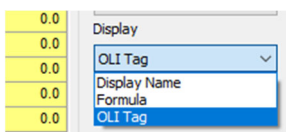
The chemistry of the brine needs to be entered. This information includes concentrations, alkalinity, pH and density. The table below describes the hypothetical water that we will create:

Brine Analysis					
Cations mg/L		Anions mg/L		Measured Properties	
Na+1	36000	Cl-	57000	Temperature	25 C
K+1	300	SO4-2	250	Pressure	1 atm
Ca2+	600	H3CO3-1	600	pH	7.67
Mg2+	150			Alkalinity	600
Sr+2	80			Density (mg/L)	1.064
Ba+2	5			Total Dissolved Solids (mg/L)	96280

The screen should look like the image below

Variable	Value	Balanced
Cations (mg/L)		
Na+1	36000.0	36116.0
K+1	300.000	300.000
Ca+2	600.000	600.000
Mg+2	150.000	150.000
Sr+2	80.0000	80.0000
Ba+2	5.00000	5.00000
Fe+2	0.0	0.0
Anions (mg/L)		
Cl-1	57000.0	57000.0
SO4-2	250.000	250.000
HCO3-1	600.000	600.000
HS-1	0.0	0.0
C2H3O2-1	0.0	0.0
Neutrals (mg/L)		
CO2	0.0	0.0
H2S	0.0	0.0
SiO2	0.0	0.0
B(OH)3	0.0	0.0

Select **Formula**



You can display an easier-to-read table by showing only the species that have actual concentrations.

Select the Show **non-zero only** box

Variable	Value	Balanced
Cations (mg/L)		
Na+1	36000.0	36116.0
K+1	300.000	300.000
Ca+2	600.000	600.000
Mg+2	150.000	150.000
Sr+2	80.0000	80.0000
Ba+2	5.00000	5.00000
Anions (mg/L)		
Cl-1	57000.0	57000.0
SO4-2	250.000	250.000
HCO3-1	600.000	600.000
Neutrals (mg/L)		

Another thing to consider is which **Balance Option** to select.

It is highly unusual for the data to be electrically neutral. Therefore, samples are reconciled for Electroneutrality. After entering each species concentrations, you will notice that Balanced values show up in the column next to values. The Column header says **Balanced**.

Variable	Value	Balanced
Cations (mg/L)		
Na+1	36000.0	36116.0
K+1	300.000	300.000
Ca+2	600.000	600.000
Mg+2	150.000	150.000
Sr+2	80.0000	80.0000
Ba+2	5.00000	5.00000
Anions (mg/L)		
Cl-1	57000.0	57000.0
SO4-2	250.000	250.000
HCO3-1	600.000	600.000
Neutrals (mg/L)		

When adding or removing ions to balance charge, the solute mass is altered. We must decide as to whether we keep the mass of the solution constant (thereby adjusting the amount of water) or keeping the amount of water constant and adjusting the solution mass.

Balance Options

Type

Dominant Ion

Dominant Ion

Prorate Cation

Prorate Anion

Makeup Ion

Select **Dominant Ion** balance option type.

You can review the Dominant Ion Charge and Ions needed to balance in the tables presented in the Summary Box.

Summary

Unit Set: [Metric \(mass concentration\)](#)

Automatic Chemistry Model

Aqueous (H+ ion) Databanks:

Aqueous (H+ ion)

No Solid phase(s)

Custom K-fit P-span

Stream Parameters:

Temperature (°C)	25.0000
Pressure (atm)	1.00000
Stream amount (L)	1.00000

Dominant Ion Charge Balance (eq/L):

Cation Charge	1.61776
Anion Charge	-1.62280
Imbalance	-5.04367e-3

Ion(s) needed to balance (mg/L):

Na+1	115.954
------	---------

Concentration Data Only.

The summary box shows additional detail about the brine's chemistry and balance option. The stream parameters table shows default values. The Dominant Ion Charge Balance shows the total cations or anions, and the total imbalance.

Now is time to enter the measured property data in the **Reconcile Tab**.

Select **Concentration Data Only** Option

Check the **Calculate Alkalinity** box

Enter the measured pH (7.67), density (1.064 g/mL) and TDS (96280 mg/L)

Leave the **Allow solids to form** unchecked.

We will leave the **Allow solids to form** unchecked because generally the industry uses acid to preserve water samples, which prevent solids to form. Acidified samples contain the unprecipitated ion concentration, which is what we entered into the brine. In this step, we will eliminate solids because allowing solids to form would change the brine's composition significantly.

Properties	Measured	Calculated
Temperature (°C)	25.0000	
Pressure (atm)	1.00000	
pH	7.67000	
Alkalinity (mg HCO ₃ /L)	600.000	
Density (g/ml)	1.06400	
Elec Cond, specific (µmho/cm)	0.0	
Total Dissolved Solids (mg/L)	96280.0	
Composition Adjustments		
Add Charge Balance (mg/L Na+1)		

Select the **Calculate** button or press the **<F9>** key

Properties	Measured	Calculated
Temperature (°C)	25.0000	
Pressure (atm)	1.00000	
pH	7.67000	7.42904
Alkalinity (mg HCO ₃ /L)	600.000	564.260
Density (g/ml)	1.06400	1.06134
Elec Cond, specific (µmho/cm)	0.0	1.26085e5
Total Dissolved Solids (mg/L)	96280.0	95090.6
Composition Adjustments		
Add Charge Balance (mg/L Na+1)		115.954

Once the calculation is done, the calculated column displays results based on the concentration that were entered in the Data Entry Tab. The calculated results of note are pH=7.43 and 564.26 mg/L as HCO₃ in total alkalinity.

Experimental inaccuracies in sample measurement may, on occasion, result in a calculation that indicates that solid is supersaturated. This can normally be ignored providing that the super saturation is not excessive.

Aqueous Phase Properties:

pH	7.42904
Ionic Strength (mol/mol)	0.0288607
Density (g/ml)	1.06134

Calc. elapsed time: 7.905 sec.
Calculation complete

The brine is supersaturated with 3 solids:
BaSO₄ (Barite), CaCO₃ (Calcite), SrCO₃ (Strontianite)
Alkalinity: 564.260mg HCO₃/L

More details of the Brine composition can be found in the **Report** Tab.

In the Report tab, scroll down to the Pre and Post Scaling Tendencies, where you will find the results of Scaling Tendencies with Solids off.

Jump to: Brine Analysis Data

Pre and Post Scaling Tendencies

Scale Mineral	Pre-scaling	Pre-index	Post-scaling	Post-index
BaCO ₃ (Witherite)	7.09380e-4	-3.14912	7.09380e-4	-3.14912
BaSO ₄ (Barite)	6.22755	0.794317	6.22755	0.794317
CaCO ₃ (Calcite)	6.35375	0.803030	6.35375	0.803030
CaSO ₄ ·2H ₂ O (Gypsum)	0.0174237	-1.75886	0.0174237	-1.75886
CaSO ₄ (Anhydrite)	0.0142718	-1.84552	0.0142718	-1.84552
KCl (Sylvite)	7.36476e-4	-3.13284	7.36476e-4	-3.13284
NaCl (Halite)	0.0324630	-1.48861	0.0324630	-1.48861
SrCO ₃ (Strontianite)	2.38156	0.376861	2.38156	0.376861
SrSO ₄ (Celestine)	0.123629	-0.907879	0.123629	-0.907879

Brine Composition

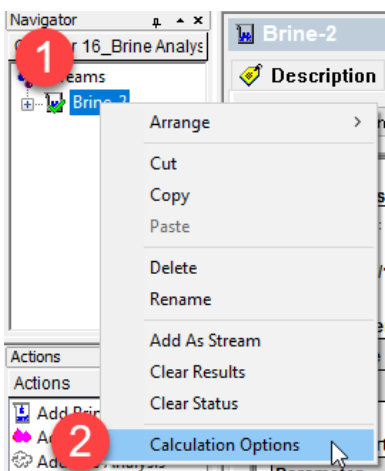
Cations	Value (mg/L)	Anions	Value (mg/L)	Neutrals	Value (mg/L)
K(+1)	300.000	Cl(-1)	57000.0		
Na(+1)	36116.0	HCO ₃ ⁻ (*)	600.000		
Ba(+2)	5.00000	SO ₄ ⁻²	250.350		
Ca(+2)	600.000				
Mg(+2)	150.000				
Sr(+2)	80.0000				

(*) This is total system carbonate including dissolved CO₂. THIS IS NOT ALKALINITY!

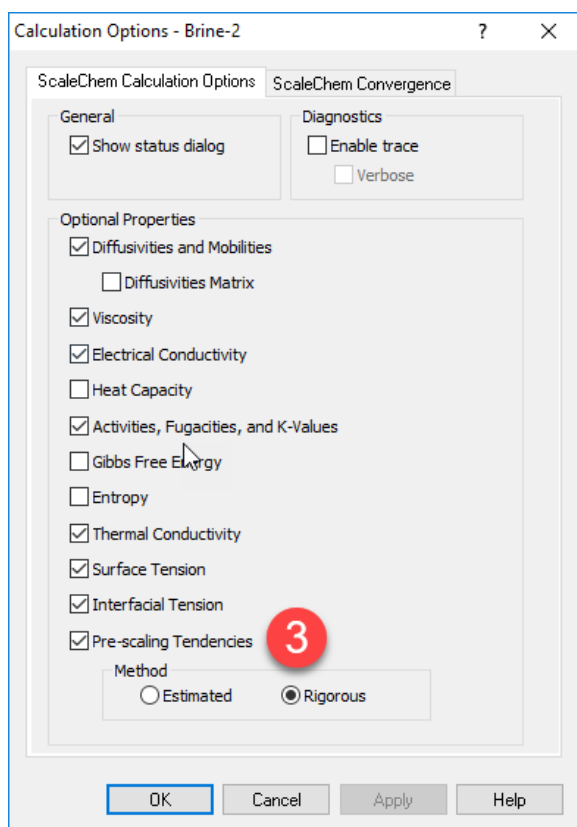
If we would have allowed solids to form, these concentrations would not be as close to the initial values.

Note: If scaling tendencies did not show up in the Report Tab, follow these steps:

- Right click on the brine analysis icon
- Select **Calculation Options**



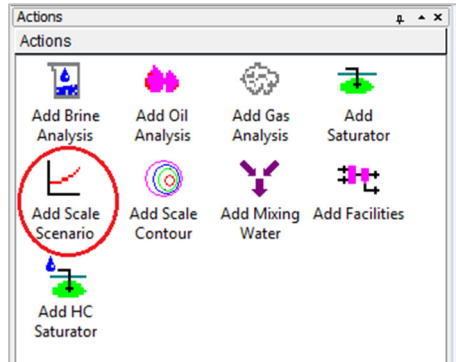
Enable *Pre-scaling Tendencies*



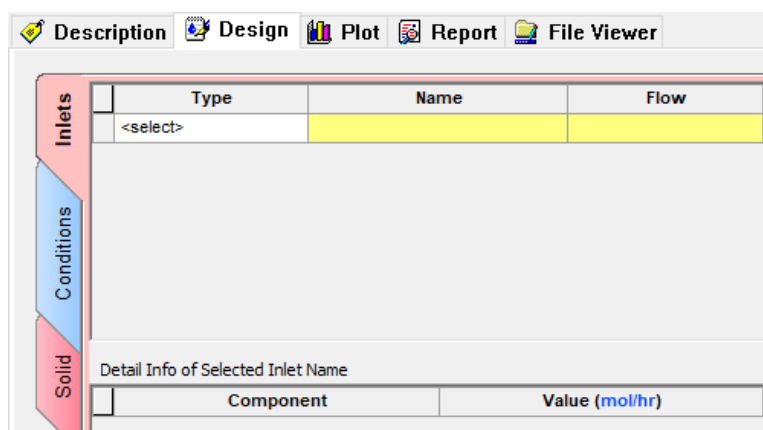
Task 2 – Create a Scaling Scenario

The next task is to calculate the brine scaling tendencies. Once the Brine Analysis data is entered and the sample reconciled, we can begin the **Scaling Scenario** calculation.

1. Select **Add Scale Scenario** from Actions panel.



Once we add a **Scale Scenario** object, the software opens to a new **Design** screen containing three vertical tabs: **Inlets**, **Conditions**, and **Solid**. We will work in each of these sections to set up the scaling calculation.



Inlet Tab

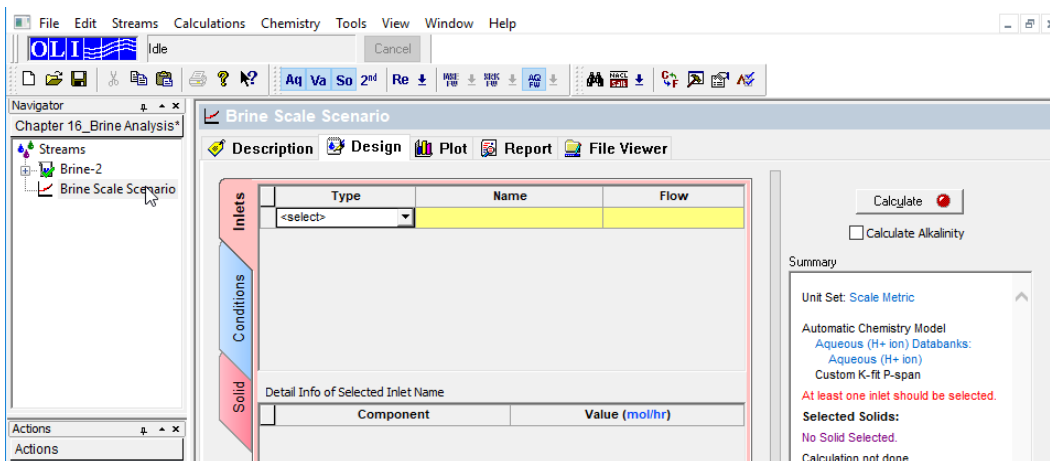
Type You can select the brine, gas or hydrocarbon of interest

Name Click in the Name field. As you position the cursor in the field, a Down Arrow will appear. You can then select from a list of brines, gases or oils already entered into this think simulation | getting the chemistry right document.

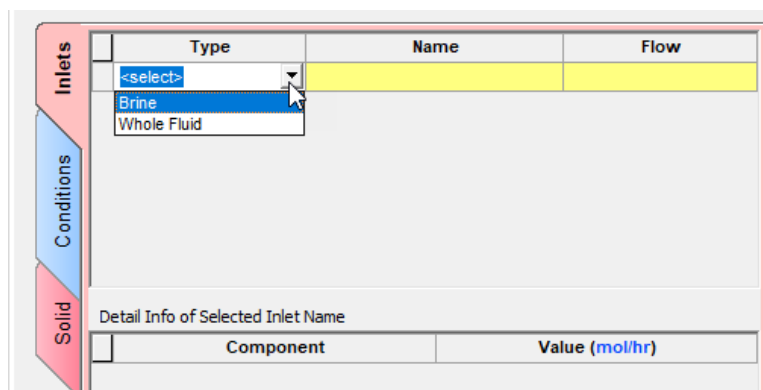
Flow Enter the flow rate for the gas, hydrocarbon or brine.

2. Click on the **Description** tab and rename the Scale Scenario as "Brine Scale Scenario".
3. Then click the **Design** tab.

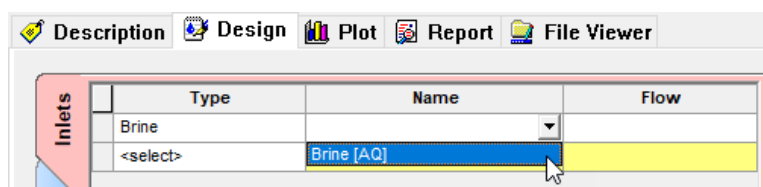
Your screen should now look like image below.



4. Select the **Inlets** tab
5. Select the right corner of the first cell in the Type column then select Brine (bbl/day). You may need to change units by clicking the blue hyperlink.



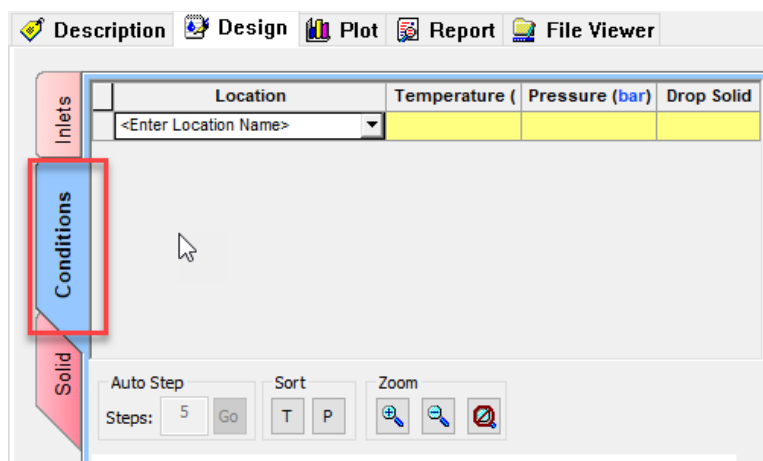
6. Select Brine from the drop-down menu in the Name column.



7. Enter 1400 (bbl/day) in the Flow Column. Please change units if necessary.

Conditions Tab

8. Select the **Conditions** Tab (vertical blue tab on the left-hand side of the Design screen)



The **Conditions** section is where we enter points along the production scheme. The first column is Location. We can use the dropdown menu in each row to select a location or type in our own location name.

9. Type in the following conditions or use the dropdown menu within the Location cells.

Scale Scenario Locations

Location	Temperature (C)	Pressure (bar)
Reservoir	125	275
Bottomhole	125	280
Downhole	115	190
Midwell	105	130
Wellhead	100	100
Choke	90	80
Separator	60	30

The diagram within the Conditions screen and the list of locations in the Summary window both show the locations in the order that we entered. This screen has options for zooming, auto steps, sorting by temperature or pressure, and dropping solids at specified conditions.

Description Design Plot Report File Viewer

Location	Temperature (°C)	Pressure (bar)	Drop Solids
Reservoir	125.000	275.000	<input type="checkbox"/>
Bottom hole	125.000	280.000	<input type="checkbox"/>
Downhole	115.000	190.000	<input type="checkbox"/>
Midwell	105.000	130.000	<input type="checkbox"/>
Wellhead	100.000	100.000	<input type="checkbox"/>
Choke	90.0000	80.0000	<input type="checkbox"/>
Separator	60.0000	30.0000	<input type="checkbox"/>
<Enter Location Name>			

Inlets: Calculate Alkalinity

Summary
 Unit Set: <Custom>
 Automatic Chemistry Model
 Aqueous (H+ ion) Databanks:
 Aqueous (H+ ion)
 Excluding 74 solid phases
 Using K-fit Polynomials
 T-span: 25.0 - 225.0
 P-span: 1.0 - 1500.0

Inlets:
 Brine (bbl/day) Brine 1400.00

Locations	Temperature (°C)	Pressure (bar)
Reservoir	125.000	275.000
Bottom hole	125.000	280.000
Downhole	115.000	190.000
Midwell	105.000	130.000
Wellhead	100.000	100.000
Choke	90.0000	80.0000
Separator	60.0000	30.0000

Selected Solids:
 No Solid Selected.
 Calculation not done

Auto Step: Steps: 5 Go Sort: T P Zoom: [Icons]

The graphical view clearly shows the five locations and their Temperature and Pressure conditions.

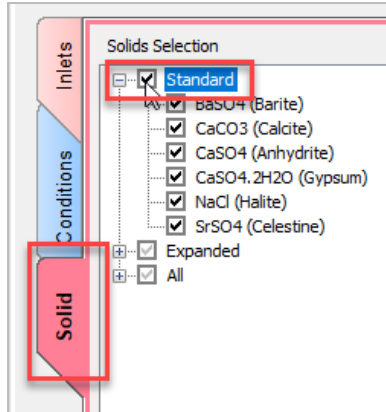
The Drop Solids checkbox column is designed to help the users decide if they want to carry forward solids from certain locations or not.

Solid Tab

10. Select the **Solid** Tab
11. Make sure that the solid button in the menu bar is selected.

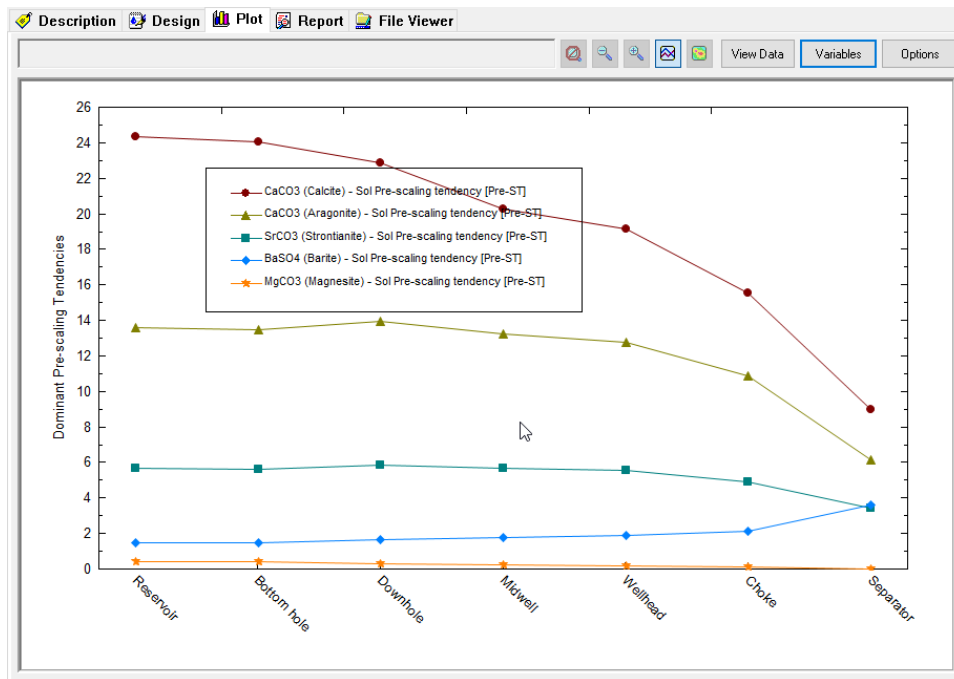


12. Select the Standard checkbox

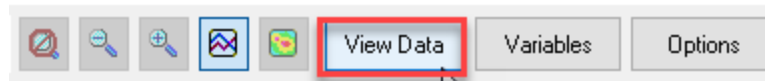


13. Press the **Calculate** button or select the <F9> key
14. Select the **Plot Tab**

You can customize which curves are visible by selecting the *Variables* button.



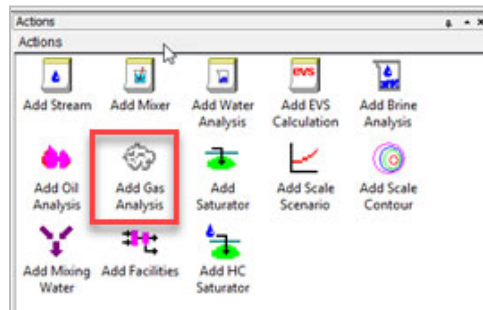
15. Select the View Data button



The *View Data* button shows the pre-scaling tendency at each location. We can copy the results of this table to a program like Excel by selecting the top left cell then selecting <Ctrl>+<C> on the keyboard.

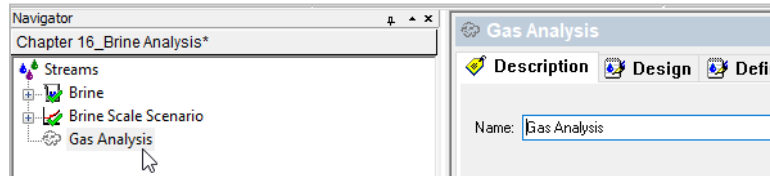
Task 3 – Create a Gas Analysis

Double click on the **Add Gas Analysis** object in the Actions Panel



This adds a Gas object to the Navigator panel.

Select the **Description** tab, then rename the object Gas Analysis.

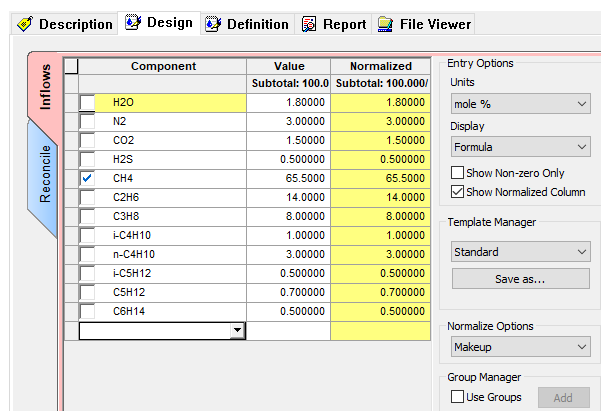


Enter the following composition and values in the Inflows grid:

Gas Analysis

Formula	Component Name	mole %	Formula	Component Name	mole %
H2O	Water	1.80	C3H8	Propane	8.00
N2	Nitrogen	3.00	i-C4H10	Isobutane	1.00
CO2	Carbon dioxide	1.50	n-C4H10	n-Butane	3.00
H2S	Hydrogen sulfide	0.50	i-C5H12	Isopentane	0.50
CH4	Methane	65.5	n-C5H12	n-Pentane	0.70
C2H6	Ethane	14.0	n-C6H14	n-Hexane	0.50

The *Inflows* grid will look like one below..



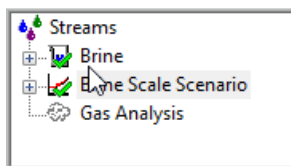
This is the extent of the gas entry step. There are modifications that can be part of the gas analysis entry step (in the Reconcile Tab), but in this case, they are not considered. Now that the gas is entered, the scale scenario considered in Task-2 will be recomputed.

Component	Normalized	Reconciled Gas
H2O	1.80000	1.75645
N2	3.00000	3.00133
CO2	1.50000	1.50066
H2S	0.500000	0.500221
CH4	65.5000	65.5290
C2H6	14.0000	14.0062
C3H8	8.00000	8.00355
i-C4H10	1.00000	1.00044
n-C4H10	3.00000	3.00133
i-C5H12	0.500000	0.500222
C5H12	0.700000	0.700310
C6H14	0.500000	0.500222

Task 4 – Recalculate Scale Scenario with Gas

The gas analysis will be added to the Scale Scenario so that it is considered during the scale evaluation.

Select the Brine Scale Scenario icon in the navigator panel



Select the **Design** Tab (horizontal tab) if not automatically sent there
 Select the **Inlets** tab (vertical) if not automatically sent there
 In the **Type** Column Add **Gas**

Type	Name	Flow
Brine (bb/day)	Brine	1400.00
Gas (std E3m3/day)		

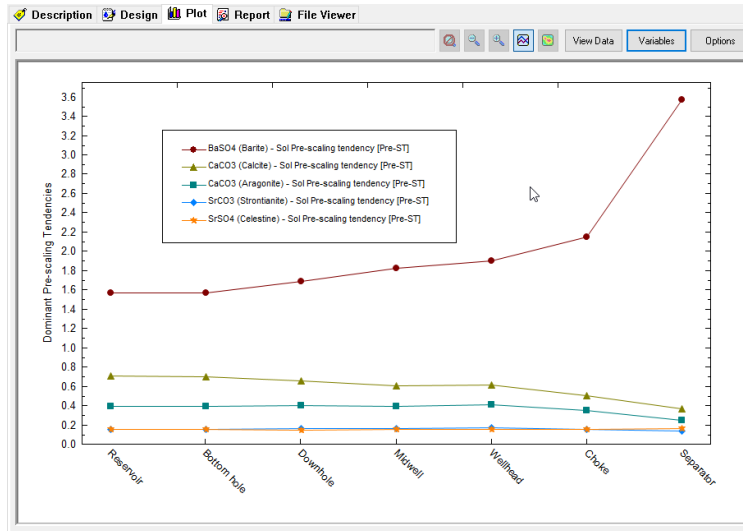
In the **Name** column select **Gas Analysis**

Type	Name	Flow
Brine (bb/day)	Brine	1400.00
Gas (std E3m3/day)	Gas Analysis	

Enter a flowrate of 250 std E3m3/day in the flow cell

Inlets	Type	Name	Flow
	Brine (bb/day)	Brine	1400.00
	Gas (std E3m3/day)	Gas Analysis	250.000
	<select>		

Calculate (Press <F9>)
Select **Plot** Tab



Select Variables button

Remove all the variables from the Y1 Axis and the Y2 axis by double-clicking on the variables (this removes them from the list). Alternatively, highlight each variable and click on the double-arrow.

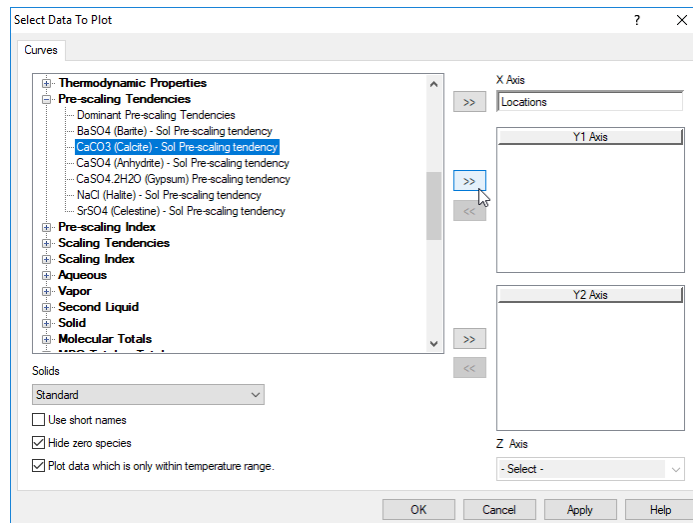
You will replace the existing variables with the calcite pre-scaling tendency.

Expand the Pre-scaling Tendencies button by clicking the + sign

Double-click on the CaCO3 (Calcite) variable to move it to the Y1 Axis

Expand the Additional Stream Parameters and add pH to the Y2 axis

Click **OK**



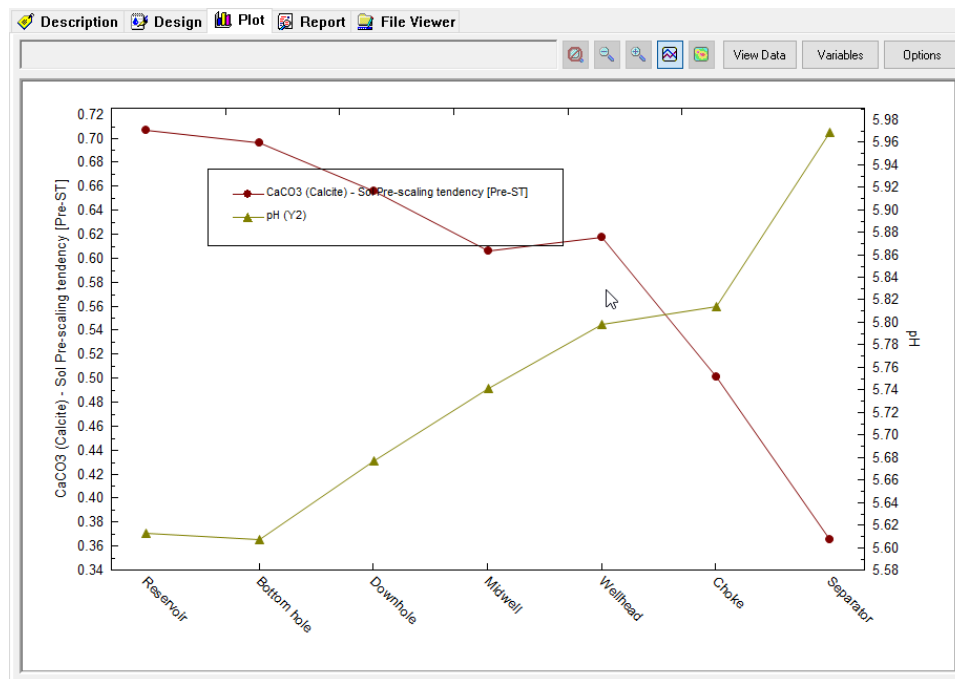
If you are in the *View Data* view, then the table should be similar to the one below.

	Locations	CaCO ₃ (Calcite) Pre-scaling tendency Scaling Tendency	pH
		Pre-ST	
1	Reservoir	0.705312	5.61211
2	Bottom hole	0.694891	5.60661
3	Downhole	0.655192	5.67654
4	Midwell	0.604697	5.74096
5	Wellhead	0.616784	5.79768
6	Choke	0.500689	5.81369
7	Separator	0.365394	5.96805

Calcite is sub-saturated ($S < 1$) at all locations.

Select the *View plot* button

The decreasing calcite saturation trend and the increasing pH is easier to see from the plot view.



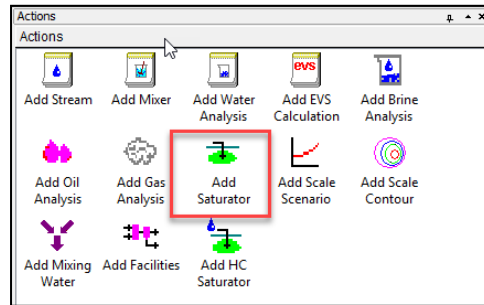
Task 5 – Creating a Saturator Object

You will use the *Saturator* object to set the reservoir minerals at equilibrium with the produced fluid. It is reasonable, in some cases, to saturate the produced fluid with common evaporite and secondary minerals like CaCO₃, CaSO₄.H₂O, FeCO₃, and NaCl. This assumes that as the reservoir fluid flows through the rock pores, there is sufficient time to interact with the surface minerals. This is based on a second assumption that the

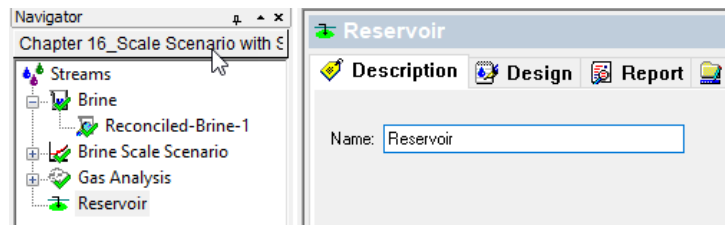
vertical column of liquid and gas are in complete equilibrium and that the saturating minerals are distributed throughout the reservoir matrix, such that complete water-mineral contact is possible.

In this case we are going to simulate a particular oil & gas well: ABC. This well produces from calcite-cemented sandstone. Barite is also present in minor quantities in the rock matrix. You will, therefore, create a reservoir called ABC Reservoir and saturate the Brine (previously calculated) with calcite and barite. You will then recalculate the Brine Scale Scenario.

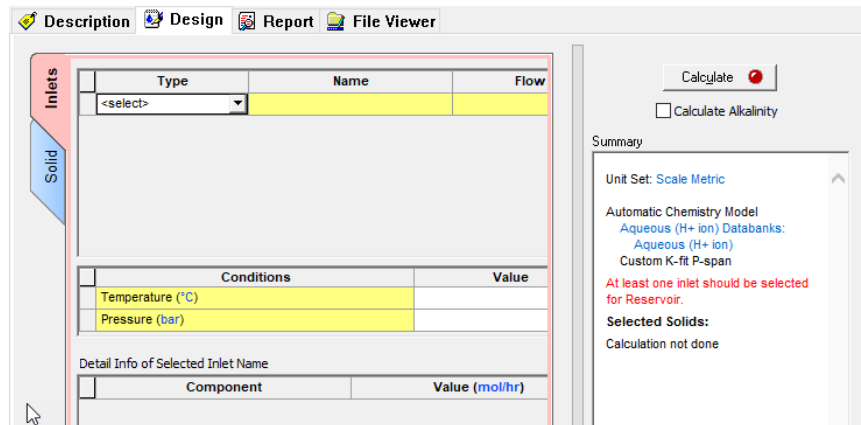
1) Add a Saturator Object



2) Select the **Description** Tab to rename the Object **Reservoir**



3) Select the **Design** Tab

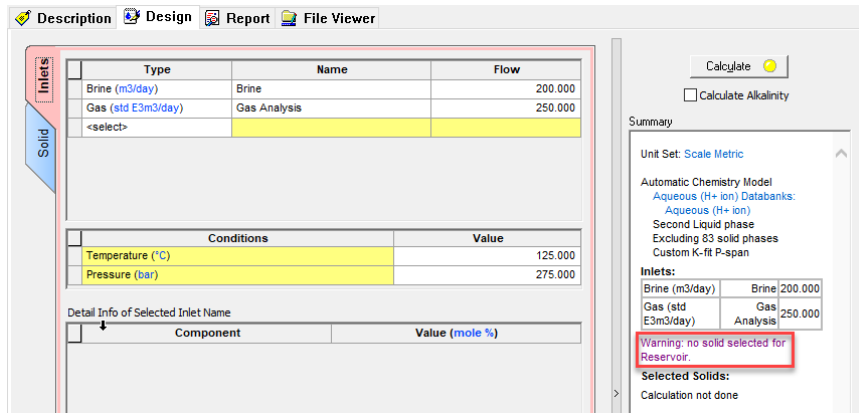


The Saturator has two vertical tabs: Inlets and Solid.

In the **Inlets** Tab the Fluids are entered in the top grid and the Conditions are entered in the bottom grid.

Solids are selected and saturated in the **Solid** Tab.

- 4) Enter the Brine calculated in Task 1 (see the image below for the flows)
- 5) Enter the Gas calculated in Task 3 (see the image below for the flows)
- 6) Enter the Reservoir conditions: 125 C and 275 bar in the conditions section.



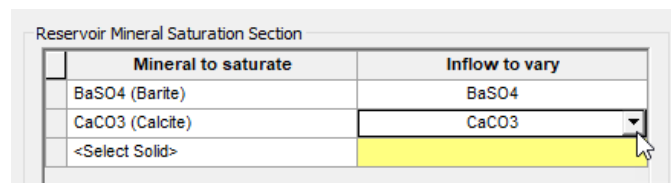
The Saturator's calculate button is yellow. This is because solids have not been selected yet. A warning also appears in the summary box. A yellow button is allowable, and a calculation may continue; it is merely a warning that the case is incomplete.

- 7) Select the **Solid** Tab (vertical tab)
- 8) Select the Standard checkbox

This last step instructs the software to allow the selected solids to precipitate – to include solid-liquid equilibrium equation in the calculation. It **does not** instruct the software to saturate these solids. Rather, if the phase is supersaturated, then it will precipitate. It is in the lower section that saturated solids are chosen.

This section contains two columns. The first (Solid) is the mineral to be saturated, and the second (inflow) is the cation and anion to be adjusted. If, for example, Barite is subsaturated in the existing fluid, then Ba+2 and SO4-2 are added. The amount of each added is stoichiometrically equivalent; one Ba+2 with one SO4-2, which maintains charge balance. If, for example, (again) Calcite is supersaturated, then equal mole amounts of Ca+2 and CO3-2 will be removed from the fluid. This inflow will be positive if the solid is subsaturated in the existing fluid, or it will be negative if the solid is supersaturated.

- 9) Use the Solid drop-down menus to select BaSO4 (Barite) and CaCO3 (Calcite) as solids to saturate
- 10) Use the Inflow drop-down menu to select BaSO4 and CaCO3 as solids to saturate (it should have been selected automatically).



At this point, the Calculate button is green indicating that the specifications are complete.

- 11) Calculate (or press the <F9> key)
- 12) Click the **Report** tab

The Saturator Report tab contains several tables: Saturation Details, Inlet Summary, Stream/Phase Properties, Pre and Post Scaling Tendencies, Brine Composition, Gas Composition, and if selected an inlet summary.

Scroll down to the Pre and Post Scaling Tendencies Table

Pre and Post Scaling Tendencies

Formula	Mineral	Excess Solute mg/L	Excess Solute lb/1000bbl	Pre-Scale S, ST	Pre-Scale SI, Index	Post-Scale S, ST	Post-Scale SI, Index
Mg(OH)2	Bruceite			4.98480e-4	-3.30235	4.98479e-4	-3.30235
NaCl	Halite	0.0	0.0	0.0245553	-1.60985	0.0245553	-1.60985
BaSO4	Barite	2.64658e-5	9.27644e-6	1.00000	1.82516e-6	1.00000	0.0
SrSO4	Celestine	0.0	0.0	0.148191	-0.829178	0.148191	-0.829178
SrCO3	Strontianite			0.209852	-0.678087	0.209852	-0.678087
CaCO3	Calcite	1.13495e-5	3.97806e-6	1.00000	-4.82687e-8	1.00000	0.0
KCl	Sylvite			2.14382e-4	-3.66881	2.14382e-4	-3.66881
CaSO4.2H2O	Gypsum	0.0	0.0	0.0179366	-1.74626	0.0179365	-1.74626
CaSO4	Anhydrite	0.0	0.0	0.0934633	-1.02936	0.0934633	-1.02936

Excess solute or Max Scale: The solids amount forming at equilibrium.

Pre-Scale: The saturation ratio before solids precipitate.

Post-Scale: The saturation ratio AFTER solids precipitate (if solids are selected).

S, ST – Saturation, Scale Tendency: The ratio of the concentration (activity) to its solubility (S=1).

SI – Scale Index: Log(S).

The Excess Solute column shows that trace amounts of BaSO4 and CaCO3 are present in the water. These exceedingly small values (in the parts-per-trillion range) are the specifications or targets for the calculation. The software sets these target solid concentrations and then adjusts up or down, the BaSO4 and CaCO3 inflows until it reaches these targets. These part-per-trillion values may look arbitrary, but in fact the values are equivalent to 1e-10 moles of solid/kg water.

Notice also, that the pre-scale tendency for BaSO4 and CaCO3 are set to 1.0, by saturation definition. That is, these are not calculated, they are defined. The remaining scale tendencies are computed.

Task 6 – Recalculate the Scale Scenario with the Saturated Reservoir

Considerable time is spent creating what is hoped to be a more representative brine. The Brine is reconciled for charge balance, and where needed, alkalinity and pH; the gas is saturated with water as needed (though not done in this case), and lastly the fluids are set to equilibrium with important reservoir minerals. It is only after these steps are complete, and that there is confidence that the assumptions and calculations are representative of the process, that a final scaling calculation is run.

The **Reservoir** calculation contains the representative fluid. It is, therefore, the output of this calculation that will be used in all subsequent calculations. To access this output, a new Type of fluid, Whole Fluid is defined. The Whole Fluid type represents 100% of the contents of a previous calculation, regardless of phase.

You will use the Whole Fluid from the Reservoir to rerun the scaling calculations.

Select *Brine Scale Scenario* in the Navigator Pane and rename it **Reservoir Scale Scenario**

Select the **Design** tab

In the **Inlets** tab in the **Type** column delete the Brine and Gas from the Type column (click the small gray box to the left of the name which will highlight the entire row, then press the delete key)

Add **Whole Fluid**

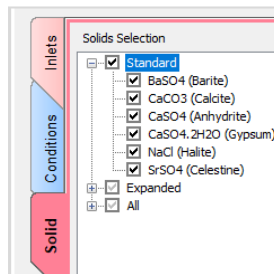
In the **Name** column select **Reservoir**

In the **Flow** column select **<Automatic>**

Description Design Plot Report File Viewer			
Inlets	Type	Name	Flow
	Whole Fluid (m3/day)	Reservoir	<Automatic>
	<select>		

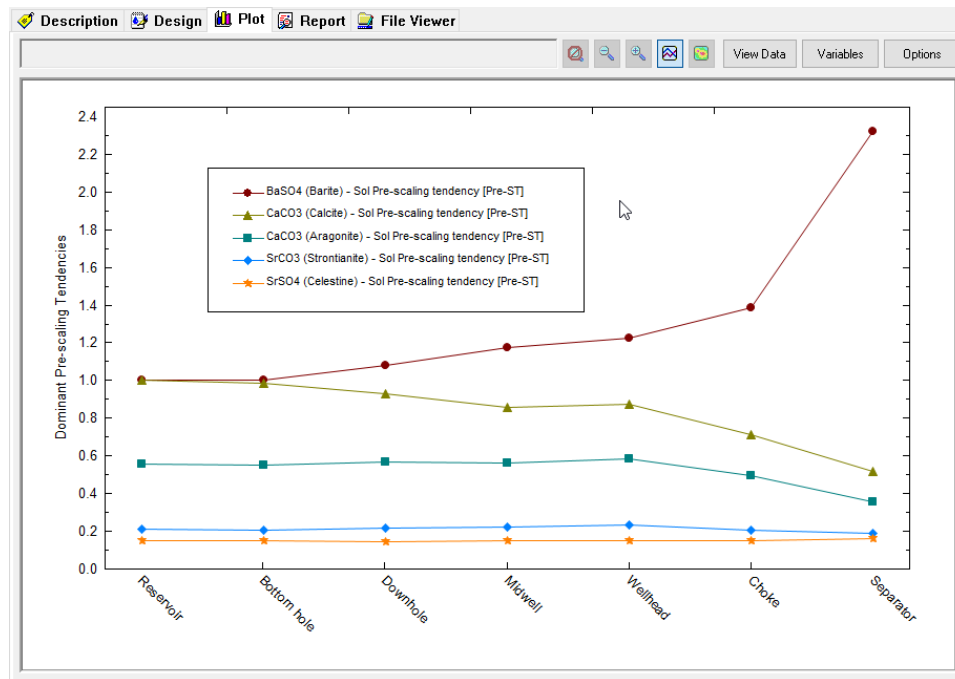
Note: The Whole Fluid type refers to all the phases within the fluid. The Automatic option takes the final flow rate phase of the separator and automatically enters this as the flow rate in the Scale Scenario calculation.

Go to the **Solid** tab and make sure that the Standard box is checked



Calculate (Press <F9>)

Select **Plot** tab and select **View Plot** (note: you may have to delete the existing entry and then reselect the dominant pre-scaling tendencies from the variables list)



The Saturator is a tool for normalizing the thermodynamics of a reservoir system. The purpose of this calculation is to apply the constraint of solid-liquid equilibrium on a system to create a specific compositional starting point.

The basis of this calculation is that water in the pores of a rock matrix is at equilibrium with the mineral surface. Some questions to consider are whether it is reasonable to assume that a reservoir gas, oil, water, and rock are in equilibrium. Furthermore, we should also consider over what vertical and radial distance we can make this claim.

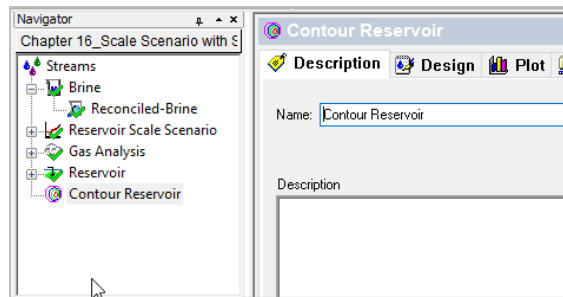
Regardless of the inconsistencies, the industry widely accepts this approach. It is up to the analyst to decide if the Saturator produces a more representative fluid than the original data.

Task 7 – Add a Contour Diagram

An alternative to the *Scale Scenario* calculation is the *Contour Diagram*. The conditions defined in the Scale Scenario are specific to production locations, and generally no more than ten are entered. By comparison, the conditions defined in the Contour Diagram are a range of temperatures and pressures. The object then computes a matrix of temperature and pressure conditions and creates a presentation-quality contour diagram.

Add Scale Contour

Rename the Object **Contour Reservoir**



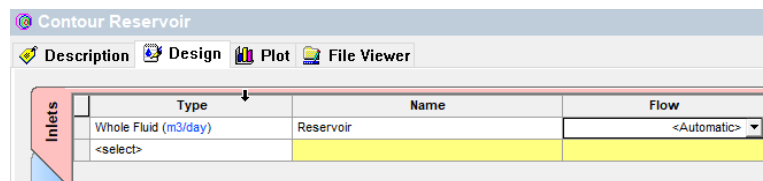
Select the **Design** Tab

Select the **Inlets** (vertical) tab

Select the bottom right corner of the 1st cell in the Inlet grid and choose **Whole Fluid**

Select **Reservoir** in the 2nd column

Keep the **<Automatic>** flow rate option in the 3rd column



Click Conditions (vertical) tab

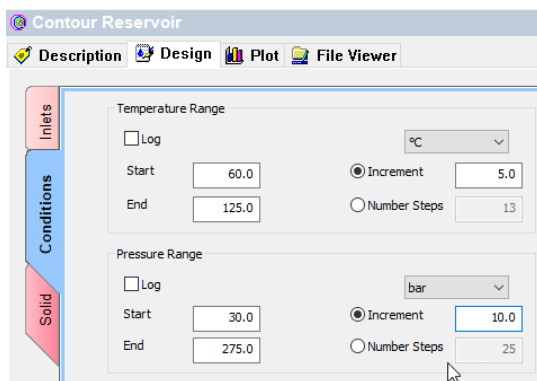
The minimum and maximum conditions are at the Separator 60C, 30 bar and Reservoir 125C, 275 bar. These are the start and end range of the study. To create a reasonable number of calculations (~300) and to keep the matrix somewhat symmetric, we will use increments of 2 C and 10 bar.

Change the Start to 60

Change the End to 125

Select the Increment radio button

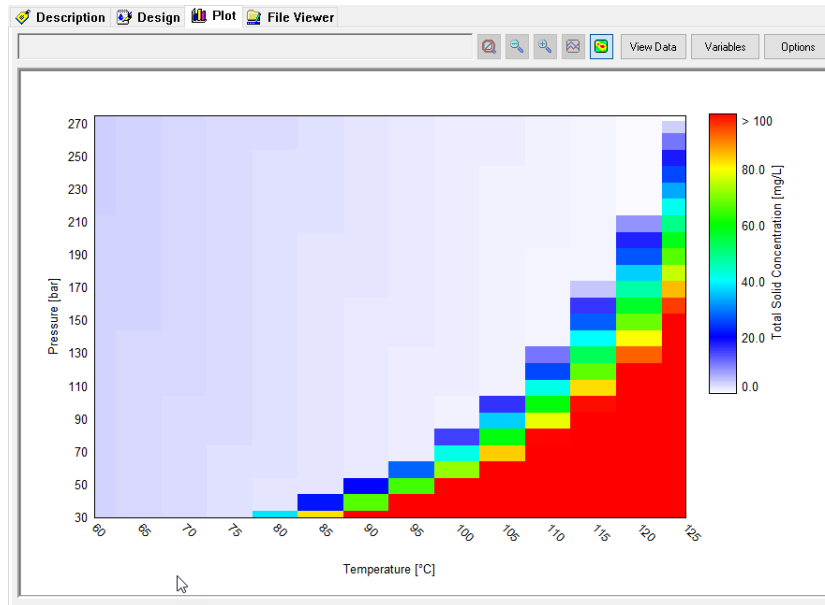
- Enter 5 as the increment
- Uncheck the Log box (if it is checked)
- In the Pressure Range box, change the Start to 30
- Change the End to 275
- Select the Increment radio button (uncheck the Log box first)
- Change the Increment to 10



This produces a matrix of 13 temperature and 15 pressure steps. This produces a 14x16 matrix, or 224 calculations.

	Temperature	Pressure
Units	°C	bar
Start	60.0	1.01325
Stop	125.0	10.1325
Step Size	5.0	0.60795
No. Steps	13.0	15.0
Calculations	224	

- Select the **Solid** Tab
- Check the Standard box
- Calculate. The calculation should take less than 5 min to complete
- When calculation is done, go to the **Plot** tab



The default plot is the total solids forming. The color scale represents a different numerical range. The red cells indicate heavier solid precipitation, and the faint purple-white in the center and left of the screen indicate that little to no scale forms. The upper right corner is the Reservoir conditions (125C and 275 bar). The lower left represents Separator conditions (60C and 30 bar). At both points, minimal solids are computed to form. The fluid traveling through the piping traverses this plot as temperature and pressure decreases. Layering production conditions (e.g., early to late life) over this plot provides an indication as to whether production will be at risk now or in the future. For example, if the pressure decline is significant (e.g., 60 bar), then the fluid will be unstable at the higher temperatures (bottom of well).

Overview of Brine, Gas and Oils and Introducing Mixer, and Saturator Objects

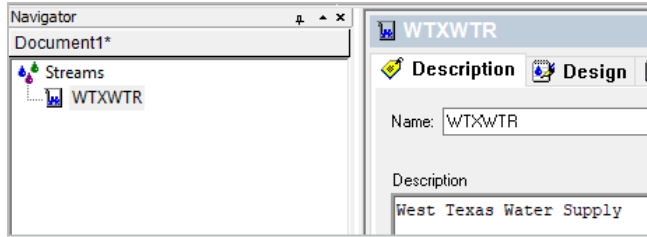
Other calculation options include the ability to mix waters at user specified ratios to find compatible waters, and the ability to saturate a water with respect to one or more solids to simulate reservoir conditions.

This chapter will cover the same calculation objects using fewer instructions and will introduce *Mixing*, *Saturator* and *Facility* Calculations. Its purpose is to reinforce what was learned in the previous chapter and to promote anticipation of next steps when using the interface.

Task 1 – Add a Brine

Add a *Brine Analysis* from the Action Panel

Rename the Brine in the **Description** Tab, and name it WTXWTR



Go to the **Design** Tab and enter the following composition in the **Data Entry** (vertical) tab:

Name: WTXWTR
 Type of water: Aquifer Water
 Comment: West Texas Water Supply

Species	Concentration
Na ⁺	3074 mg/L
Ca ⁺²	910 mg/L
Mg ⁺²	249 mg/L
Fe ⁺²	0.77 mg/L
Cl ⁻¹	4474 mg/L
SO ₄ ⁻²	2960 mg/L
HCO ₃ ⁻	439 mg/L
HS ⁻¹	146.2 mg/L

Check the *Show non-zero Only* box (under Entry Options)

Go to the **Reconcile** (vertical) tab

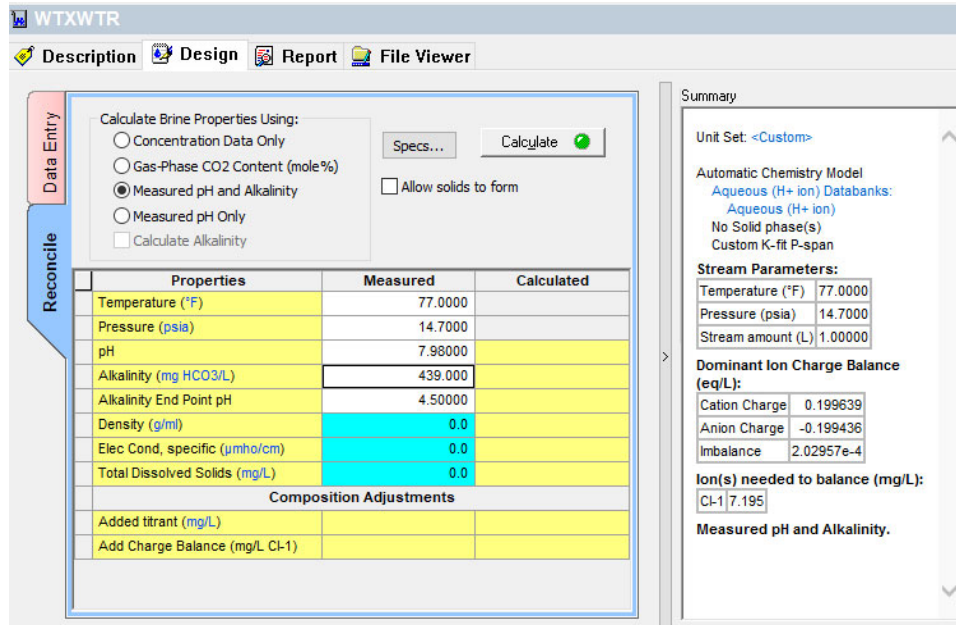
Select the measured pH and alkalinity Option

Enter the following conditions (change units if necessary)

- To change units just click on the hyperlink next to the variable that you want to change.



Temperature	77 F
Pressure	14.7 psia
pH	7.98
Alkalinity end Point pH	439 mg/L as HCO ₃ ⁻
Titration pH	4.5
Density	(will be estimated)

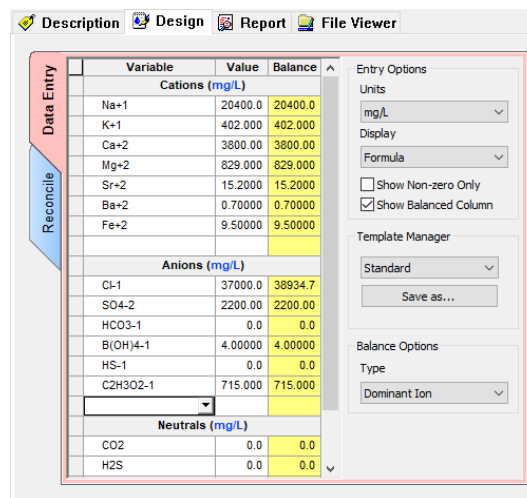


Click the **Calculate** Button

Task 2 – Add a Second Brine

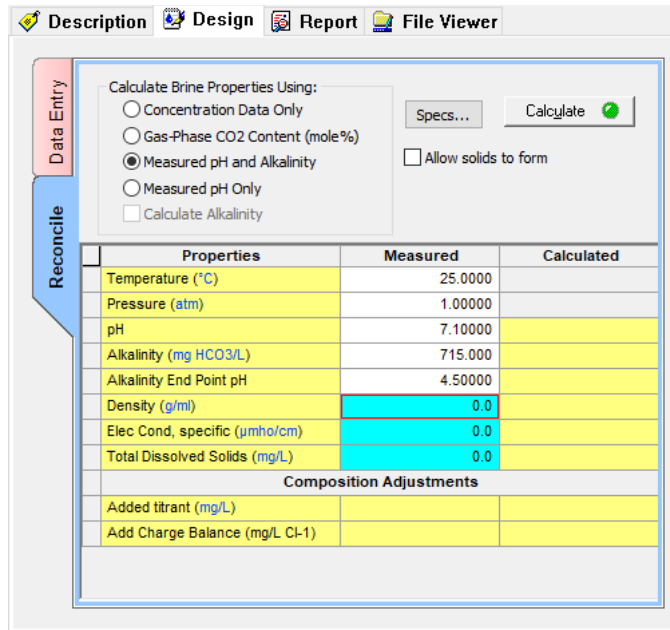
Add a Brine Analysis, name it SSC-Brine

Enter the composition given below in the **Data Entry** (vertical) Tab



Go to **Reconcile** tab

Select **pH and Alkalinity** calculation type, and enter the information provided in the figure below.

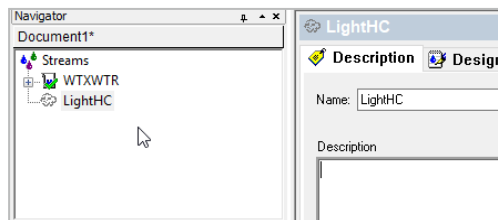


Click the Calculate button

Task 3 – Add a Gas

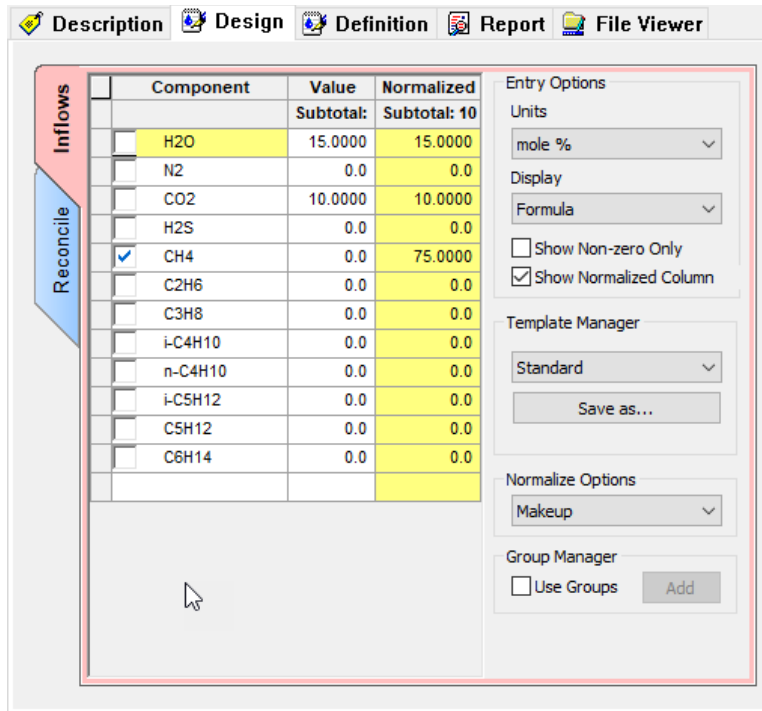
From the Actions Panel click on *Add Gas Analysis*

Input the name in the **Description** tab. Name it *LightHC*



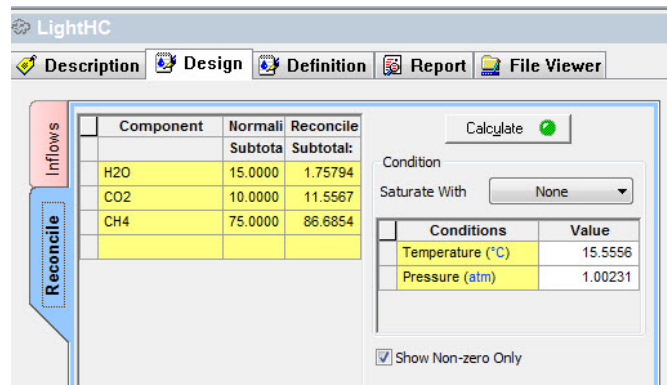
Go to the **Design** Tab and enter the following composition in the **Inflows** (vertical) tab
Enter the following composition:

Component	Composition
Carbon dioxide (CO ₂)	10 mole %
Water (H ₂ O)	15 mole %



think simulation | getting the chemistry right will assume that all of the hydrocarbon gas is methane (CH4). So, in this case the software normalizes the gas adding 75 mole% of CH4.

Go to the **Reconcile** (vertical) Tab

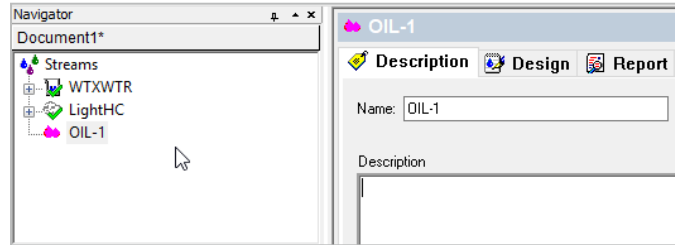


Leave the default conditions for Temperature and Pressure
Calculate

Task 4 – Add an Oil

From the Actions Panel click *Add Oil Analysis*.

Enter the name in the **Description** Tab. Name it *OIL-1*



Go to the **Design** tab

This tab is divided into:

Combined Tab: Here pure components (organic and inorganic) are entered.

Pseudocomponent Tab

Assay Tab: Here distillation curves are entered.

Reconcile Tab

For this example, we will enter pure component and pseudocomponent data.

Go to the **Combined** tab

Enter the following composition:

Methane (CH ₄)	20.53mole %
Hexane (C ₆ H ₁₄)	8.595mole %
CO ₂	6.09mole %

Note: You will have to scroll down to find the CO₂ entry.

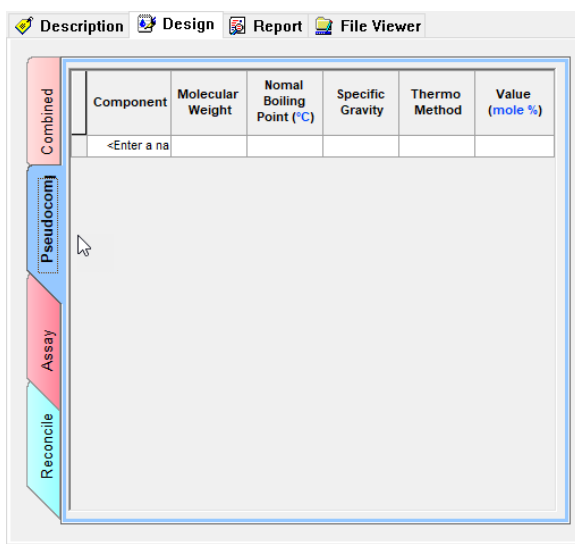
The screenshot shows the software interface with the 'Design' tab selected. The 'Combined' tab is active, displaying a table of components and their values. The 'Summary' panel on the right shows the unit set and stream parameters.

Component	Value	Normalized
Inflows		
H ₂ O	0.0	0.0
CH ₄	20.5300	58.2990
C ₆ H ₁₄	8.59500	24.4072
CO ₂	6.09000	17.2938
Subtotal		100.0

Entry Options:
Units: mole %
Display: Formula
 Show Non-zero Only
 Show Normalized Column
Template Manager: Standard
Normalize Options: Prorate

Summary:
Unit Set: Metric (mole fraction)
Automatic Chemistry Model: AQ (H+ ion) Databanks: Public
Stream Parameters:
Temperature (°C): 15.0000
Pressure (atm): 1.00000
Prorate Normalization.
Normalized Summary (mole %):
Inflows: 100.000
Pseudocomponents: 0.0
Assay: 0.0
Equilibrium Calculation.

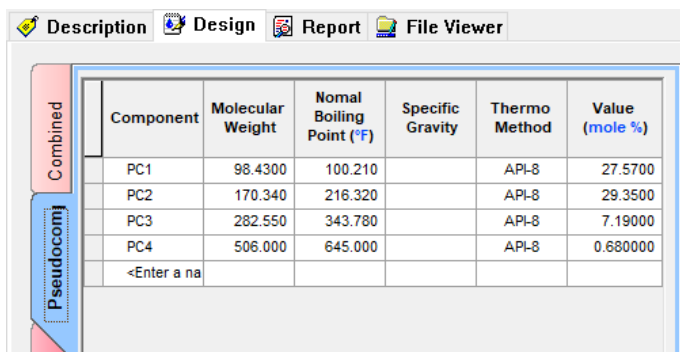
Go to the **Pseudocomponent** tab



Add the following pseudocomponents:

Name	MW (g/mol)	nBP (F)	Thermo Method	Value mole %
PC1	98.43	100.21	API	27.57
PC2	170.34	216.32	API	29.35
PC3	282.55	343.78	API	7.19
PC4	506.0	645.00	API	0.68

The completed input looks like this:

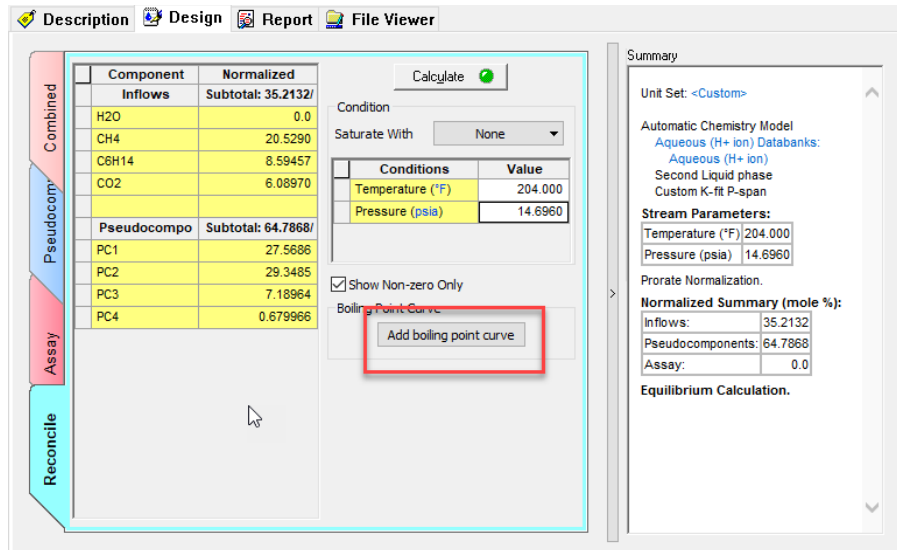


Go to the **Reconcile** (vertical) tab

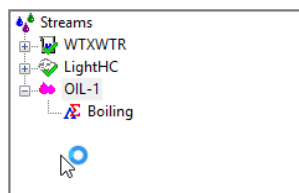
Here you will see how well the pseudocomponent will predict the phase behavior of the hydrocarbon sample.

In the Condition option (below calculate button) enter T=204 F and P=1 atm.

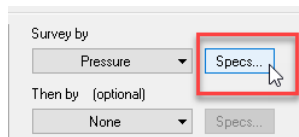
Click on the *Add boiling point curve* (red square shown)



A new calculation appears in the navigation panel below OIL1 Object.



This is a survey by Pressure. Click on the specs button and specify the conditions below. Change pressure units if necessary.

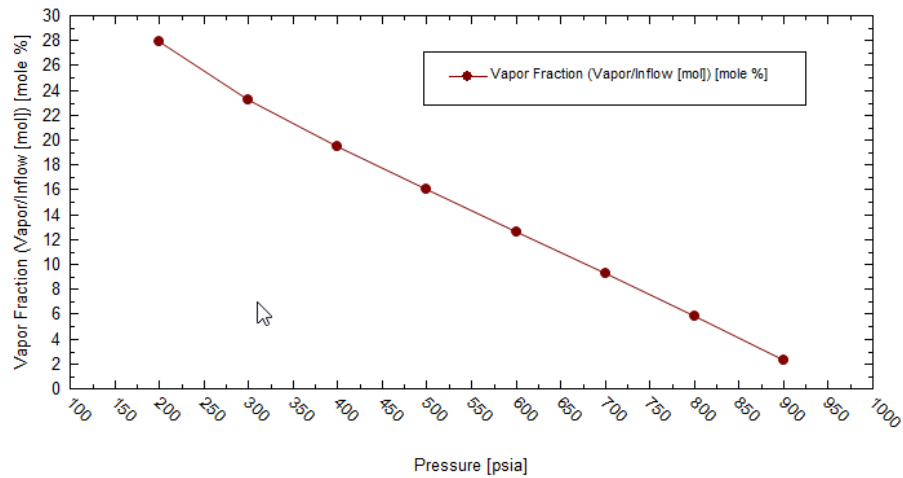


Enter a pressure range:

Start 200 psia
 End 2000 psia
 Decrement 100 psia

Click the **Calculate** button.

Click on the plot tab, you will see the following graph: You could adjust the parameters by clicking on curves.

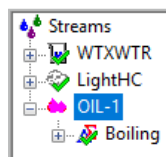


If the curve does not meet expectations, you will have to adjust the mole percentages or the pseudocomponent properties. This is a manual iterative approach. You can see the actual data by clicking the View data button.

	Pressure	Vapor Fraction (Vapor/Inflow [mol])
	psia	mole %
1	200.000	27.8711
2	300.000	23.1977
3	400.000	19.4660
4	500.000	16.0216
5	600.000	12.6532
6	700.000	9.26672
7	800.000	5.80919
8	900.000	2.24433
9	1000.00	
10	1100.00	
11	1200.00	
12	1300.00	
13	1400.00	
14	1500.00	
15	1600.00	
16	1700.00	
17	1800.00	
18	1900.00	
19	2000.00	

Frequently the hydrocarbon is saturated with water. We will simulate this part.

Go back to OIL-1 in the Action panel



Click on the **Design** tab

In the Conditions option use T= 77 F and 14.7 psia.

Click on the **Calculate** button.

When done, the software will create a *Reconciled OIL-1* in the Navigator pane.

The Brine, Gas and Oil that we already calculated will be used for the upcoming Mixer, Saturator and Facilities Calculations.

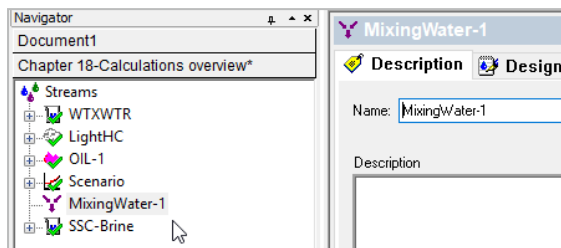
Task 5 – Adding a Mixer Calculation

The Mixer calculation determines if two waters (brines) can be mixed. Frequently the mixing of two waters will cause precipitates to form which were not present in original brines. This can lead to the plugging of a formation when an injection water is mixed with the natural fluids in the formation.

From the Actions Panel, click on the Add Mixing Water logo.



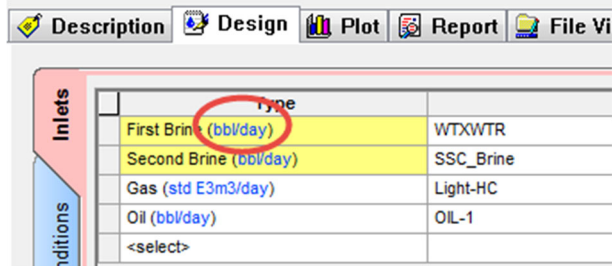
After double clicking the logo, you will see the object in the Navigation Panel.



Click on the **Design** tab to enter more information.

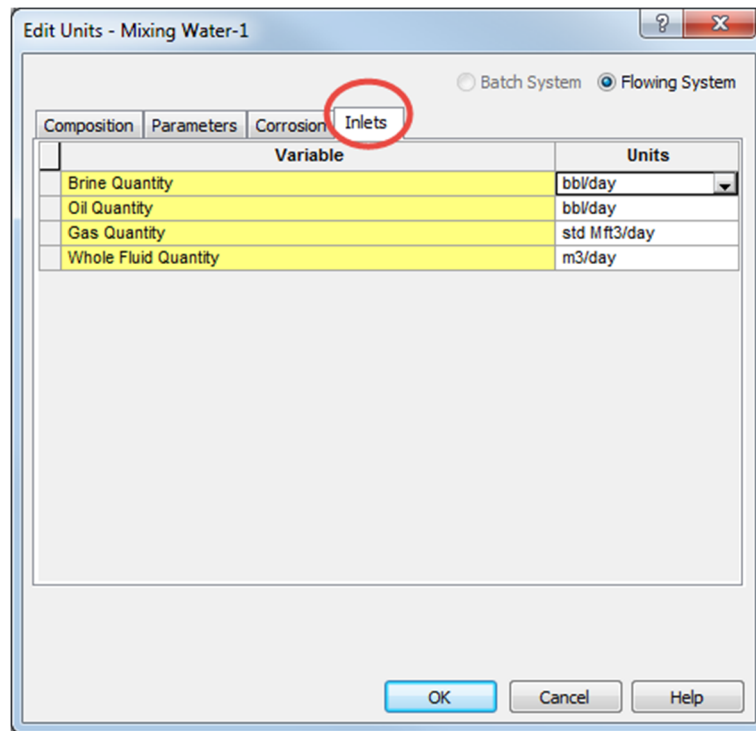
Select your Brines, Gas and Oil s as shown in the figure below. Enter the indicated brine flow rate of 1000 bbl/day, gas flow of 230 stdMft3/day and oil flow of 7 bbl/day.

Note: To change units on brine, oil and gas, click on the hyperlinked ([blue](#)) units inside of the bracket next to Inlets First Brine, Second Brine etc. This is under the column heading Type.

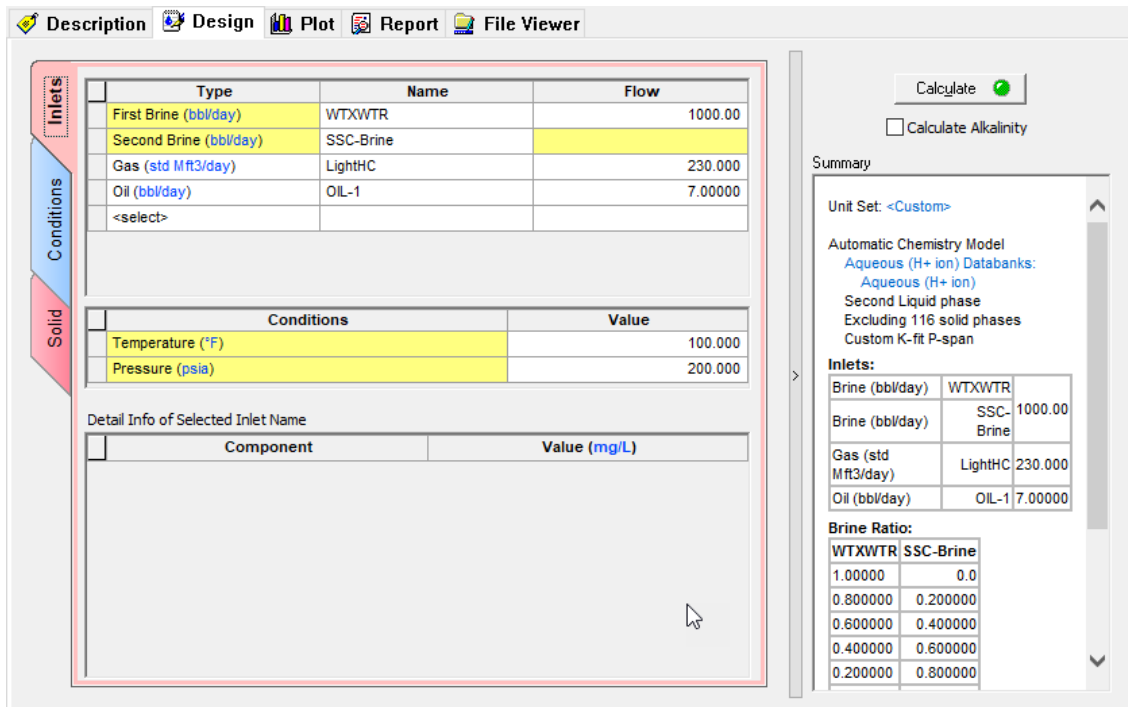


This should pop the following window up. Click on Inlets tab and change the units.

Inlets tab looks like below. Changing units on Brine:



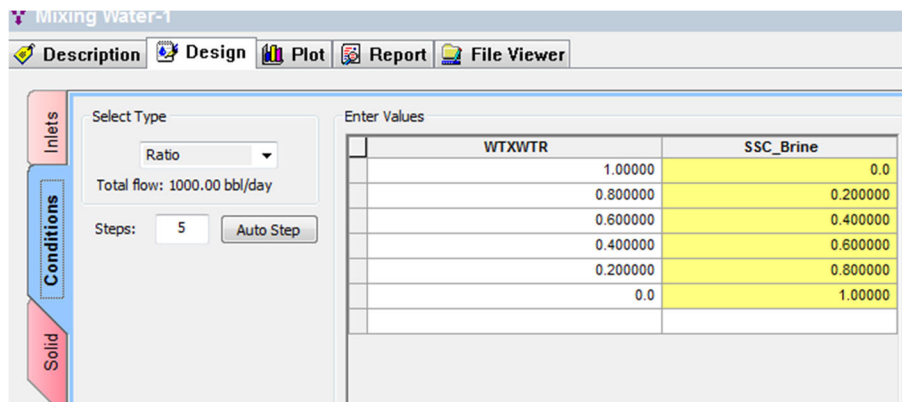
The final Mixer with inflows entered should look like the image below:



Go to the **Conditions** tab.

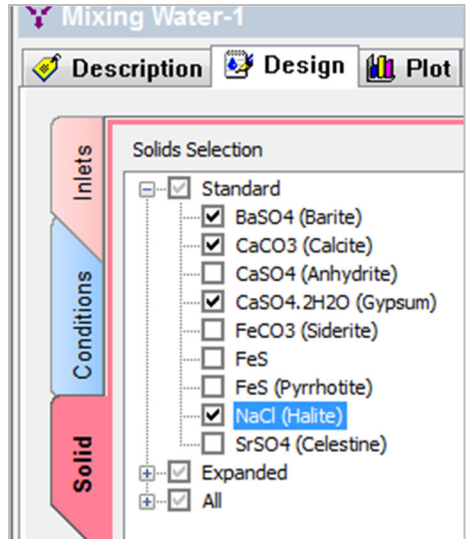
In this example, we are mixing the brines at 100 F and 200 psia. The first brine specified (WTXWTR) is the one we compare to when evaluating the ratios. In this case we start out with all brine WTXWTR and none of the SSC_Brine and end up with none of brine WTXWTR and all of the SSC_Brine.

Leave the default values



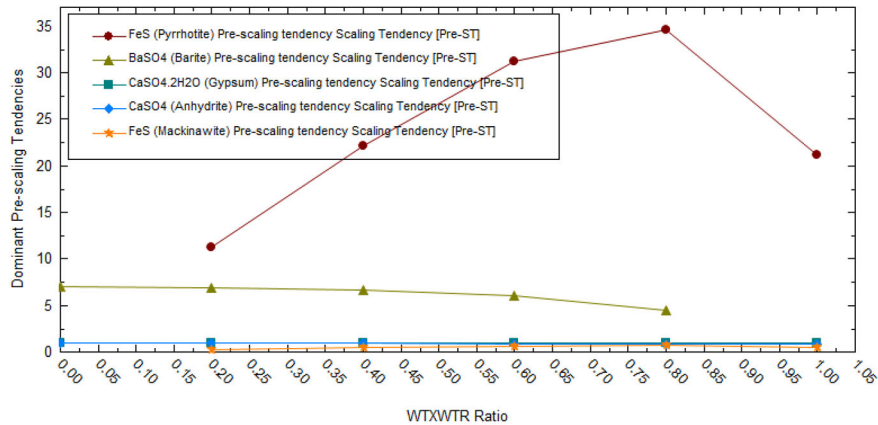
Go to the **Solid** tab

For this calculation we are only selecting a few of the possible solids. Mark a check box next to desired solids (BaSO4, CaCO3, CaSO4.2H2O, NaCl).

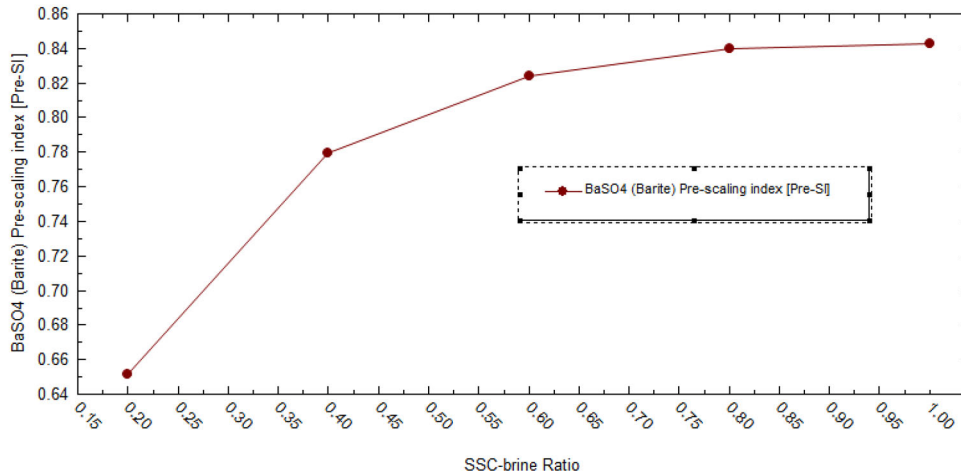


Click on the Calculate button.

Click on the **Plot** tab.



To study the effects better go to the variables button and eliminate other solids precipitated by the << arrow. Keep only one solid (in this case BaSO4). The ratio is relative to the first brine specified. This means at a ratio of 0.0 (all the first brine and none of the second) we have no BaSO4 scaling. As we add the second brine, the amount of BaSO4 increases. These waters are perhaps incompatible.

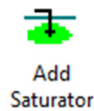


Task 5 – Adding a Saturator Calculation

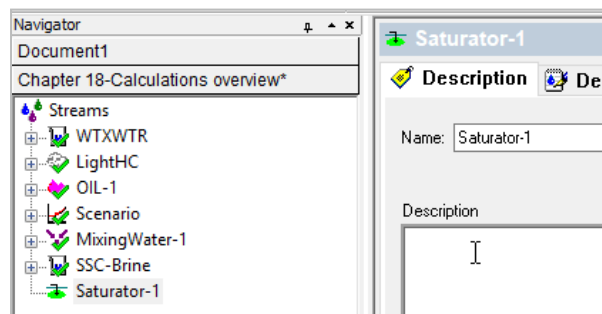
Water and gas samples at the surface are not necessarily representative of conditions in the reservoir. The processing of the samples may involve significant changes in the chemistry.

The Saturate option (often referred to as "Saturate at reservoir conditions") allows the user to "Back-calculate" the conditions downhole.

Select **Add Saturator** from the Actions Panel.



Rename the object in the descriptions tab. Name it Saturator-1



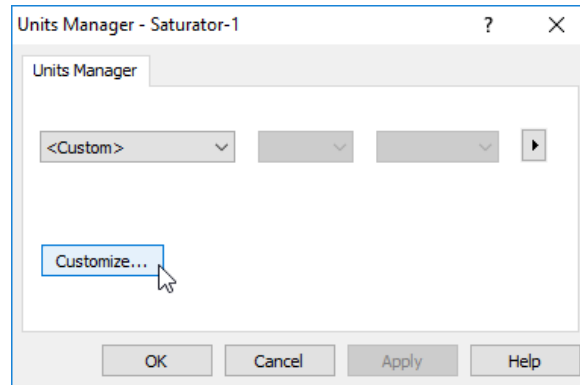
Go to **Design** tab

And go to **Inlets** (vertical) tab

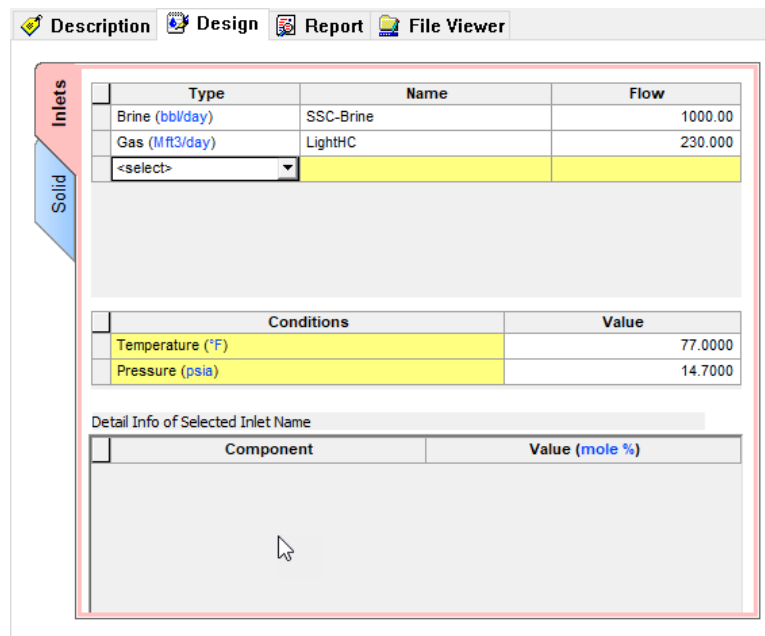
We will select objects that we have already defined.

Enter a Brine flow of 1000 bbl/day (SSC-brine)
 Enter a Gas flow of 230 std Mft3/day (LightHC)
 Enter T=77 F and P=14.7 psia

Set these units as custom units for all new objects in Units manager.



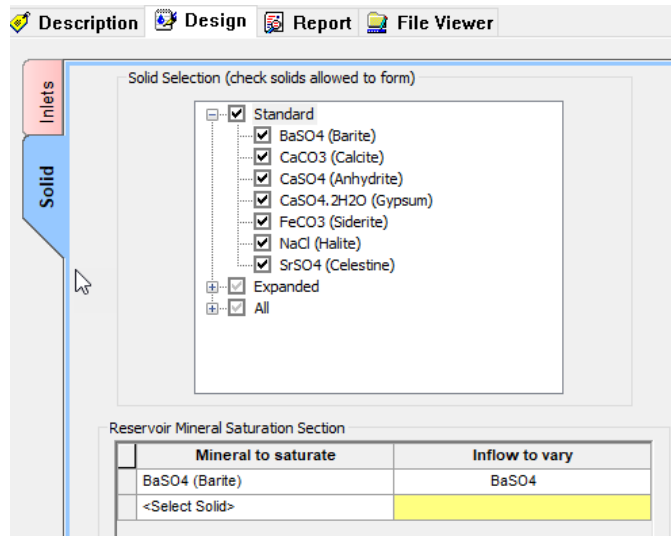
The window should look like the image below.



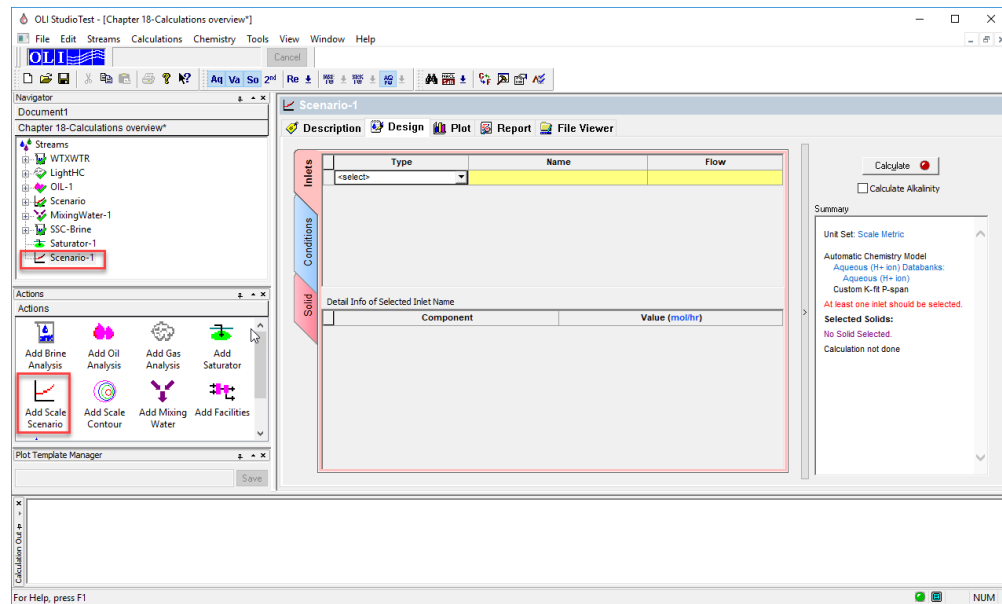
Go to **Solid** (vertical) tab
 Check the Standard box

We need to select solids inflow to vary for Saturator1. Under the table *Select Mineral to saturrate*, choose the solid to vary from the dropdown list.

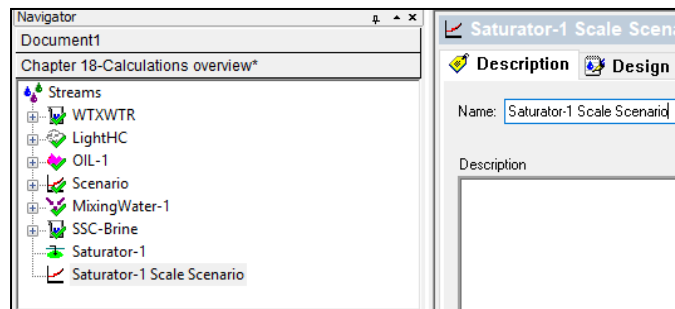
Select BaSO4 (solid) and hit enter. Automatically the inflow to vary BaSO4 will appear.



To study the Saturator-1 (Brine and Gas mix) at various locations we need to add a Scaling Scenario object.



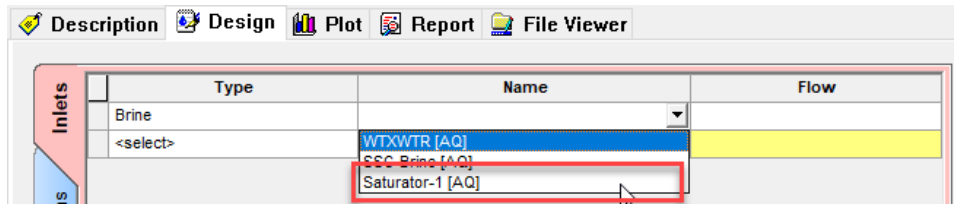
Name the new Scale Scenario as *Saturator-1 Scale Scenario* under the **Description** tab.



Go to the **Design** Tab

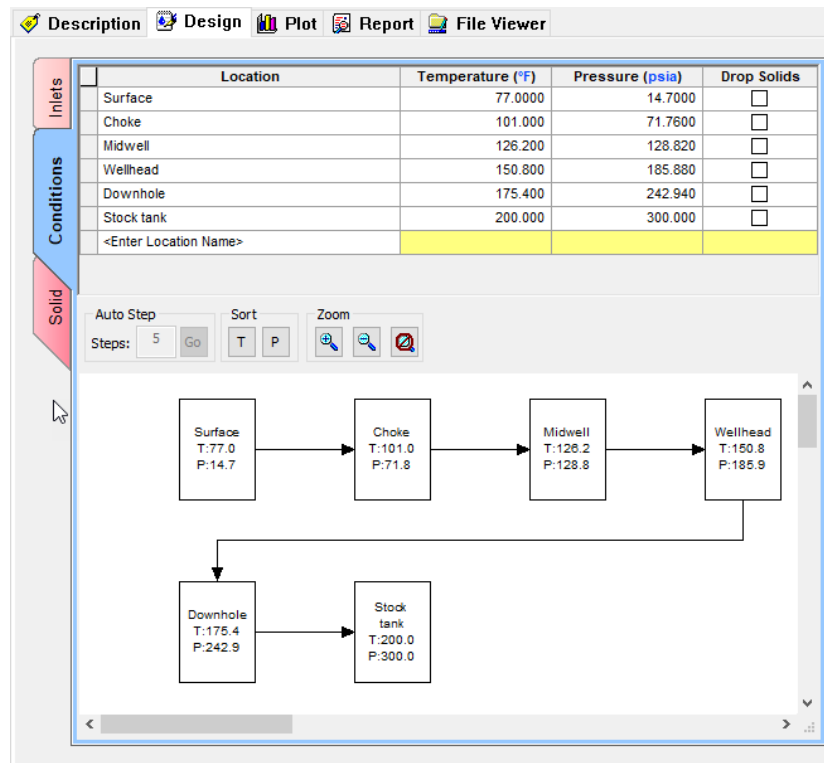
Under the **Inlets** (vertical) tab, select *Brine* under the *Type* column

Make sure to select Saturator-1, as is shown in the picture below:



Flow will be automatically controlled. Locations can be input under the **Conditions** tab.

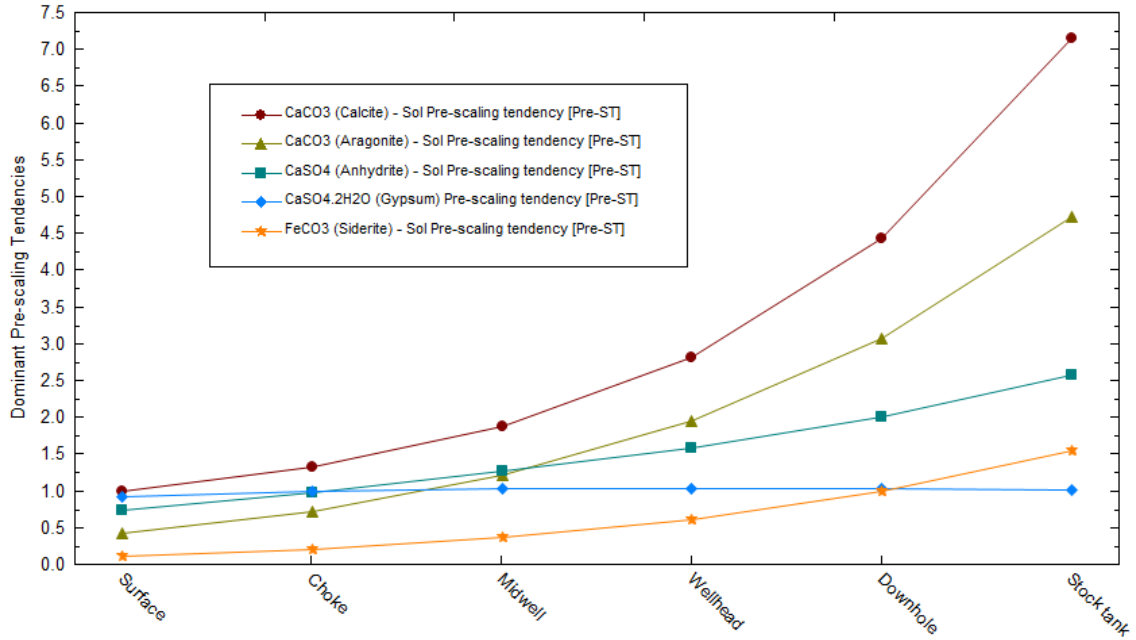
Go to **Conditions** (vertical) tab, and enter the information provided in the figure below:



Go to **Solid** tab and check the Standard box

Click the Calculate Button

Go to **Plot** tab



After the calculation is complete, the plot for scale scenario shows that other solids are appearing.

Go to the **Report** tab, and look for Pre and Post Scaling Tendencies

Pre and Post Scaling Tendencies

Formula	Mineral	Excess Solute		Pre-Scale		Post-Scale	
		mg/L	lb/1000bbl	S, ST	SI, Index	S, ST	SI, Index
CaSO4.2H2O	Gypsum	0.0	0.0	0.928262	-0.0323294	0.928262	-0.0323294
FeCO3	Siderite	0.0	0.0	0.114350	-0.941763	0.114350	-0.941763
SrSO4	Celestine	0.0	0.0	0.203747	-0.690908	0.203747	-0.690908
SrCO3	Strontianite			0.0120481	-1.91908	0.0120481	-1.91908
BaSO4	Barite	0.0	0.0	1.00000	-2.23307e-11	1.00000	0.0
CaSO4	Anhydrite	0.0	0.0	0.731753	-0.135635	0.731753	-0.135635
CaCO3	Calcite	0.0	0.0	1.00000	-1.46285e-11	1.00000	0.0
NaCl	Halite	0.0	0.0	0.0121174	-1.91659	0.0121174	-1.91659
KCl	Sylvite			6.71059e-4	-3.17324	6.71059e-4	-3.17324

Excess solute or Max Scale: The solids amount forming at equilibrium.

Pre-Scale: The saturation ratio before solids precipitate.

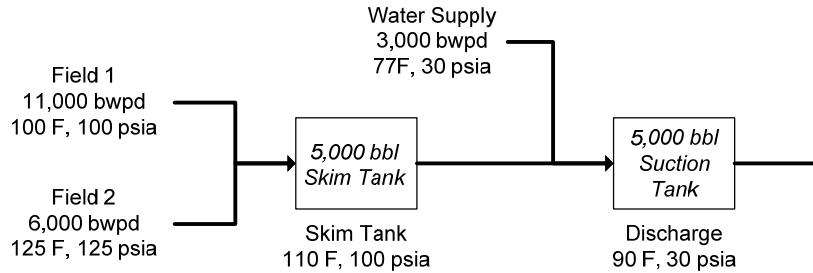
Post-Scale: The saturation ratio AFTER solids precipitate (if solids are selected).

S, ST – Saturation, Scale Tendency: The ratio of the concentration (activity) to its solubility (S=1).

SI – Scale Index: Log(S).

Introducing the Facilities Object

This section presents a new calculation object: *Facilities*. The Facilities is a simplified process simulator; it mixes and separates. think simulation | getting the chemistry right has the ability to link together several individual calculations to create a flow sheet facility. An example of a facility calculation is shown in the figure below.



It is a simple process in which two field brines mix in a skim tank. The discharge from this tank then mixes with a water supply in a discharge tank. Below are the compositions and conditions of the inlet fluids.

Name	Field 1 mg/L	Field 2 mg/L	Water Supply mg/L
Na+	38209	27078	3074
Ca+2	6600	4480	910
Mg+2	1531	1191	249
Fe+2	120	6.6	0.77
Cl-1	73150	51134	4474
SO4-2	2453	1840	2960
HCO3-	421	677	439
HS-1	244	146.2	0
Conditions			
Temperature	100 F	125 F	77 F
Pressure	100 psia	125 psia	30 psia
pH	6.97	7.53	7.98
Alkalinity (As HCO3 mg/L)	421	677	439
Alkalinity End Point pH	4.5	4.5	4.5

Follow the steps below:

Open a new Window for Simulation

Create the above brines: Field 1, Field 2 and Water Supply

Use the *Add Brine Analysis* object as you have done before to create them.

The **Data Entry** Windows should look like this:

Variable	Value	Balanced
Cations (mg/L)		
Na+1	38209.0	38370.4
K+1	0.0	0.0
Ca+2	6600.00	6600.00
Mg+2	1531.00	1531.00
Sr+2	0.0	0.0
Ba+2	0.0	0.0
Fe+2	120.000	120.000
Anions (mg/L)		
Cl-1	73150.0	73150.0
SO4-2	2453.00	2453.00
HCO3-1	421.000	421.000
HS-1	244.000	244.000
C2H3O2-1	0.0	0.0
Neutrals (mg/L)		
CO2	0.0	0.0
H2S	0.0	0.0
SiO2	0.0	0.0

Variable	Value	Balanced
Cations (mg/L)		
K+1	0.0	0.0
Ca+2	4480.00	4480.00
Mg+2	1191.00	1191.00
Sr+2	0.0	0.0
Ba+2	0.0	0.0
Fe+2	6.60000	6.60000
Anions (mg/L)		
Cl-1	51134.0	51257.9
SO4-2	1840.00	1840.00
HCO3-1	677.000	677.000
HS-1	146.200	146.200
C2H3O2-1	0.0	0.0
Neutrals (mg/L)		
CO2	0.0	0.0
H2S	0.0	0.0
SiO2	0.0	0.0
B(OH)3	0.0	0.0

Variable	Value	Balanced
Cations (mg/L)		
K+1	0.0	0.0
Ca+2	910.000	910.000
Mg+2	249.000	249.000
Sr+2	0.0	0.0
Ba+2	0.0	0.0
Fe+2	0.770000	0.770000
Anions (mg/L)		
Cl-1	4474.00	4637.91
SO4-2	2960.00	2960.00
HCO3-1	439.000	439.000
HS-1	0.0	0.0
C2H3O2-1	0.0	0.0
Neutrals (mg/L)		
CO2	0.0	0.0
H2S	0.0	0.0
SiO2	0.0	0.0
B(OH)3	0.0	0.0

Reconcile these three brines for measured pH and alkalinity.

Make sure that the *Allow solids to form* box is uncheck at the bottom of the reconciliation options for all the brines.

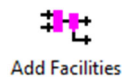
Calculate Brine Properties Using:

- Concentration Data Only
- Gas-Phase CO2 Content (mole%)
- Measured pH and Alkalinity
- Measured pH Only
- Calculate Alkalinity

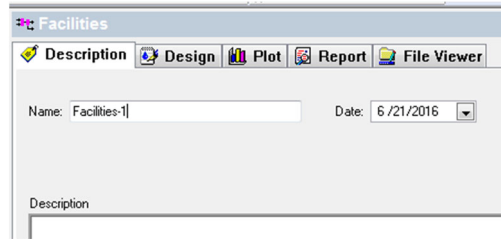
Allow solids to form

Properties	Measured	Calculated
Temperature (°F)	100.000	
Pressure (psia)	100.000	
pH	6.97000	6.97000
Alkalinity (mg HCO3/L)	421.000	420.990
Alkalinity End Point pH	4.50000	
Density (g/ml)	0.0	1.07666
Elec Cond, specific (µmho/cm)	0.0	1.84894e5
Total Dissolved Solids (mg/L)	0.0	1.22617e5
Composition Adjustments		
Added titrant (mg/L) HCl		227.307
Add carbonate (mg/L CO2)		-238.440
Add Charge Balance (mg/L Na+1)		161.374

Select **Add Facilities** from the Action Panel.



Go to the **Description** Tab and rename the object as Facilities-1

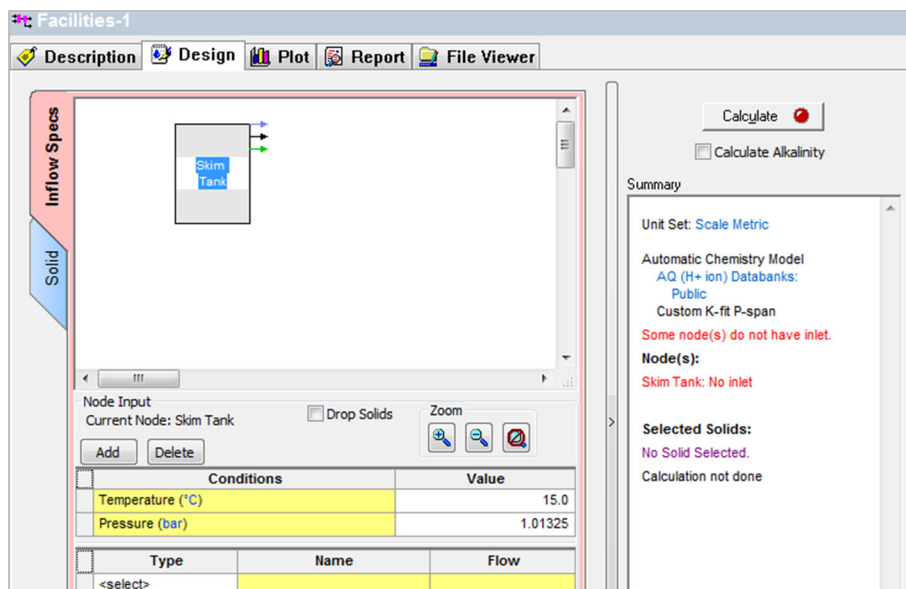


The facilities calculation is based upon transferring information between calculations through nodes. These nodes can be thought of as pseudo brines and gases. These pseudo brines are not stored as individual brine rather they are used internally in the calculation. The concentration and flow rates for these nodes can be viewed in the output.

Go to the **Design** tab
 Go to the **Inflow Specs** (vertical tab)

Within **Inflow Specs**, we can add Nodes via Node input options. There will be one default node added.

Double click on the node name (where it says: Node 1) and type "Skim Tank".

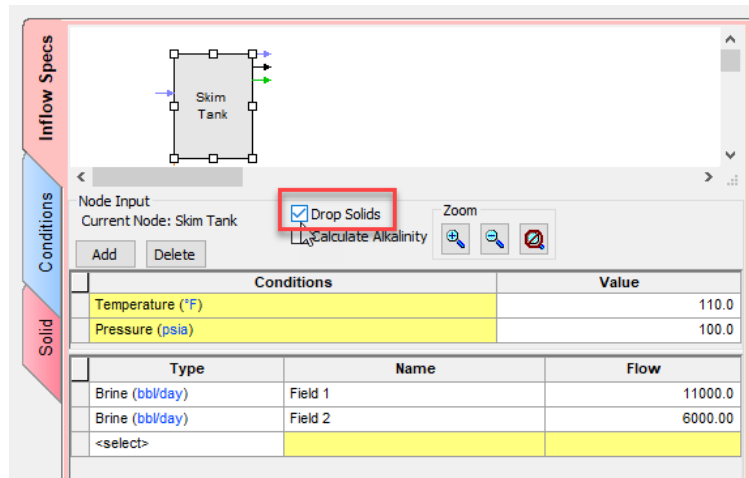


Enter the name, description, conditions, and streams for the Skim Tank shown in the table below:

	Flow	Temperature, F	Pressure, psia
Field 1	11000 bbl/day	100	100
Field 2	6000 bbl/day	125	125
Water Supply	3000 bbl/day	77	30
Skim Tank	5000 bbl/day	110	100
Suction Tank	5000 bbl/day	90	30

Make sure to select drop solids checkbox at the Skim Tank node.

When complete, your screen should look like this.



The output of this calculation will go to the next node.

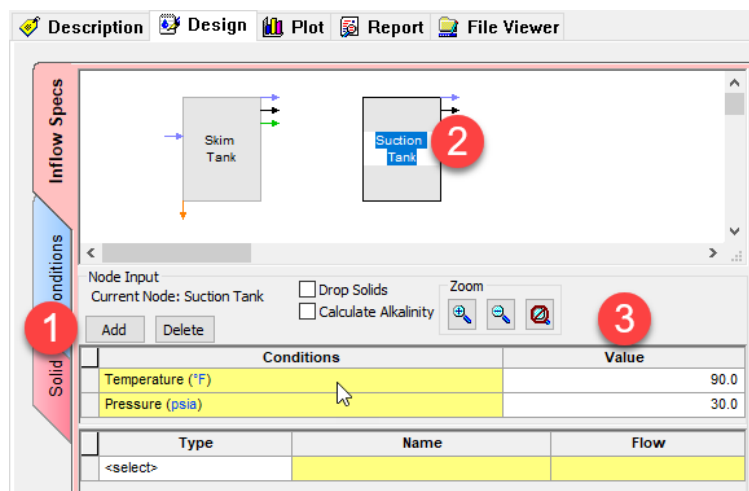
Next, enter the information for the second node, Suction Tank. We will select the output brine of the Skim tank, which is a **brine from node**. The temperature and pressure as well as the flow of the brine are calculated.

Click on the Add button to add a second Node

Change the name of the node to Suction Tank

Change the conditions of this node to 90 F and 30 psia.

When complete your screen should look like the image below:



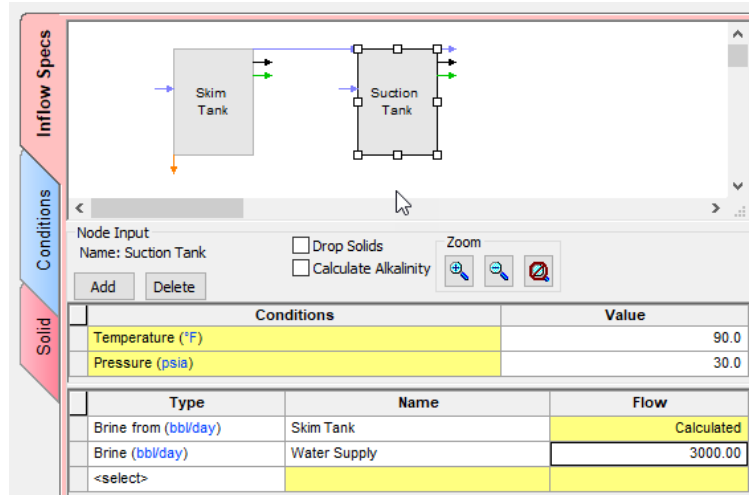
When a brine is calculated in a facilities calculation, we have the option of allowing any produced solids to be considered (that is they traveled along with the brine) or to **eliminate** them as they precipitate out. We will eliminate the solids in this case. The orange downward arrow from Skim Tank indicate dropped solids.

We are also adding the **Water Supply** to this tank.

In the Type column and first row select *Brine from*. In the Name column select *Skim Tank*. The *Flow* is calculated (since it comes from the Skim Tank).

In the Type column and second row select *Brine*. In the Name column select *Water Supply*. Enter 3000 bbl/day in the Flow column.

When complete the screen should look like the image below.



Click on the Calculate button, or press <Ctrl+F9>

Go to the **Report** tab, and check for the Pre-scaling Tendencies and Scaling Tendencies

See the Results

Pre-Scaling Tendencies

Column Filter Applied: Values > 1.0e-4

Temperature Filter Applied: Active TRange Only.

Nodes	CaCO3 (Aragonite)	CaCO3 (Calcite)	CaSO4.2H2O (Gypsum)	CaSO4 (Anhydrite)	FeCO3 (Siderite)	Fe(OH)2 (Amakinite)
Temp Range °C	Invalid	Invalid	Invalid	Invalid	Invalid	Invalid
Skim Tank	5.20710	8.91186	1.24207	1.39847	0.165109	3.48775e-4
Suction Tank	4.83533	9.86145	1.18226	1.09089	0.147451	1.58132e-4

Nodes	FeS (Pyrrhotite)	FeS (Mackinawite)	MgCO3.3H2O (Nesquehonite)	MgCO3 (Magnesite)	Mg(OH)2 (Brucite)	MgSO4.7H2O (Epsomite)
Temp Range °C	Invalid	Invalid	Invalid	Invalid	Invalid	Invalid
Skim Tank	41958.3	906.834	4.47209e-3	9.15709e-3	1.05810e-3	1.11430e-3
Suction Tank	41552.1	781.107	3.37396e-3	4.74809e-3	3.15204e-4	1.21290e-3

Based on these results, it is clear to see that the software predicts the formation of several solids in this process. Solids with a Pre-Scaling Tendency > 1 are predicted to form.

Chapter VI – Scaling Inhibition

Introduction

OLI has developed a rigorous Nucleation and Inhibition tool for mineral scaling formation. The two tools help users predict the onset of precipitation in a process environment and also how to delay it. Both tools are built on OLI's fundamental thermodynamic framework and extends these predictions into kinetics using the Classical Nucleation Theory [ref]. This theory use the energetics of the solution and the solid to predict the time needed for a supersaturated solution to start precipitating. This is the transition time between when a metastable solution finally starts to precipitate. The background and details of nucleation is offered by Wikipedia: https://en.wikipedia.org/wiki/Classical_nucleation_theory

What is a mineral scale?

Mineral scaling occurs when there are changes in process conditions, such as pressure and temperature changes, dissolved gases, or when mixing incompatible waters. When scales accumulate in fixed diameter volumes, like membrane pores, production tubing, or process piping, flow is restricted. Action is then needed to remove the scale and restore flow.

A scale deposit may occur as single mineral phases, but more commonly, it is a combination of different elements. Common scales include CaCO₃ (calcite) and BaSO₄ (barite) in oil and gas production, CaCO₃, struvite, Ca₃(PO₄)₂, Mg-Silicates, and silica in water treatment, Jarosite, CaSO₄, and CaCO₃ (calcite) in mineral processing, and additional scale types in other chemical processes.

Scale deposition involves two distinct steps. The first is the nucleation step, this is the time between when a supersaturated water goes from no solids to forming the stable, microscopic crystals. The second is the crystal growth step. In this step, the microscopic crystals grow until the concentration in the water reduces to the point where the solution is no longer supersaturated.

The duration of this nucleation step is known as the “induction time”. It is the time that passes from the creation of supersaturated solution to the detection of first solids. This time is critical, because the longer this time can be delayed the greater chance that the solids do not form in an area that affects operations.

Scale formation - how OLI predicts this induction time?

OLI has developed a state-of-the-art tool that predicts this induction time. This enables users to assess the risk of mineral scale forming more accurately in their process. This is a major advancement compared to existing technology, in which the scaling tendency value plus empirical rules of thumb are used to assess scale risk in a process.

Figure 2 is a plot showing the output of the new model. The x-axis is the inverse square of the Scale Index. The scale index is a base-10, logarithm of the scale tendency.

$$SI^{-2} = (\log_{10}(ST))^{\frac{1}{2}}$$

A lower SI⁻² value (left side of the plot) means a higher supersaturation.

The Y-axis is the time it takes before stable crystals begin to form (in seconds). As the liquid supersaturation increases (increasing the driving force for precipitation), the time it takes for the solids to form shrinks.

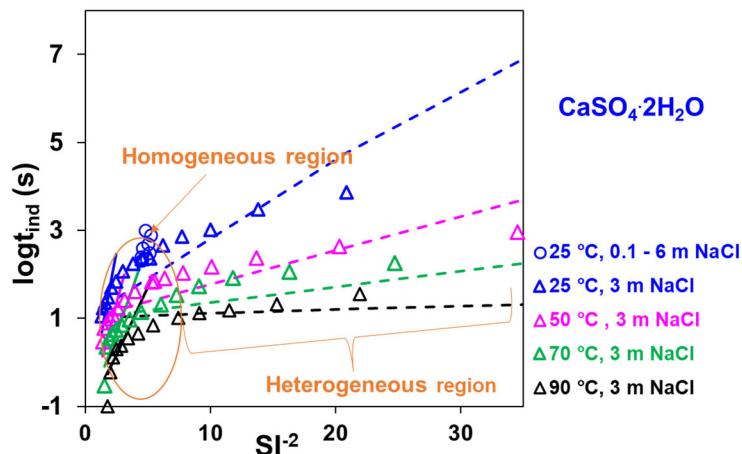


Figure 0-1 - Calculated and experimental gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) induction times in the CaSO_4 -NaCl solution at 25, 50, 70, and 90 °C. Symbols are experimental data, whereas lines represent MSE+CNT model calculations

There are two distinct slopes to the plot, the far-left slope is the Homogeneous nucleation region, while the right slope is the heterogeneous region. The homogeneous nucleation region represents a liquid that is highly supersaturated, and where little time elapses before solids start precipitating. The heterogeneous region is where the liquid is only slightly saturated, and solids only start to form if there is dust or other types of particles in the water that makes it easier for the solids to form. Both time regions are important to modeling induction time properly, and the OLI database contains the required parameters for these calculations.

V11.5 Nucleation Induction Time model

OLI Studio V11.5 is the first delivery of this new technology. We have created a database that will predict the induction time for four of the most common scales, calcite (CaCO_3), barite (BaSO_4), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), and Celestine (SrSO_4). In future releases, the predictions will be extended to other solids.

Scale Inhibition - how OLI is used to predict treatment?

Scale inhibitors are a type of chemical that interacts with the nascent crystallites and prevents them from becoming stable. They effectively delay the formation of a stable crystal by poisoning its surface. Scale inhibitors are an essential part of engineering, because when added to the process water, they delay the formation of these crystals, allowing a process to remain free of solids. Scale inhibitors are used in many applications, including cooling tower water, as a pre-treatment to RO membranes, and oil and gas production wells.

Because scale inhibitors represent the key solution to unwanted mineral scaling, OLI created a database that predicts this time delay. Thus, an OLI Studio user can now predict a more accurate scale risk analysis for their process and simultaneously develop a chemical treatment plan. Six of the most common scale inhibitors are

included in the V11.5 software; NTMP/ATMP, DTPMP, HEDP, EDTPMP, PPCSA, and PMA (see footnote for chemical names)¹¹.

Using the Nucleation Model in OLI Studio

The nucleation model is a post-process to all OLI calculations. Therefore, the only impact on any calculation is that a new table will be available in the Report tab, or a new set of categories will be available in the Plots tab. When scale inhibitors are added, then its speciation is included in the calculation. Usually the inhibitor concentrations are low (in the parts per million) so there will be minimal performance difference. There will be the same changes to the report and plot, since the inhibitor speciation will be added to the output, and its effects on nucleation will also be shown.

Performing induction time calculations in V11.5

The V11.5 release contains nucleation induction times (t_{ind}) for four mineral phases; CaCO_3 (calcite), BaSO_4 (barite), SrSO_4 (celestine), and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (Gypsum). The release also contains inhibition t_{ind} for six scale inhibitors, HEDP, NTMP/ATMP, DTPMP, EDTMP, PMA, and PBTC. The nucleation model is developed in the MSE framework (database) and its prediction range extends across the range of this framework.

OLI Tag Name	Chemical Formula	IUPAC Names
DTPMP	C9H28N3O15P5	Diethylenetriamine penta(methylene phosphonic acid)
HEDP	C2H8O7P2	1-hydroxyethane 1,1-diphosphonic acid
NTMP/ATMP	C3H12NO9P3	Nitritotris(methylenephosphoric acid)
PMLA	C40H40O40	Poly maleic acid
PBTC	C7H11O9P	2-phosphono-butane-1,2,4-tricarboxylic acid
EDTMP	C6H20N2O12P4	Ethylenediamine tetra(methylene phosphonic acid)

¹¹ 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP), amino tris (methylenephosphonic acid) (NTMP), diethylenetriamine penta (methylene phosphonic acid) DTPMP, ethylenediamine tetra (methylene phosphonic acid) (EDTPMP), and polymaleic acid (PMA)

Setting up the automatic calculation

Induction time calculations are activated within the **Calculation Options** popup window (Figure 0-2). When checked, the model sub-routine is included as a post process to the calculation being run. The induction time calculation is available for the Single Point and Survey calculation of a Stream, in a Mixer calculation, and in the five ScaleChem calculations (Saturator, Scale Scenario, Facilities, Contour, Mixing Waters).

Start the software. There should be no streams or calculations in the Navigator panel

Select Tools>Options>Calculation Options

Check the **Scaling Induction Time(s)** box at the bottom of the popup window. Then press OK to close the window.

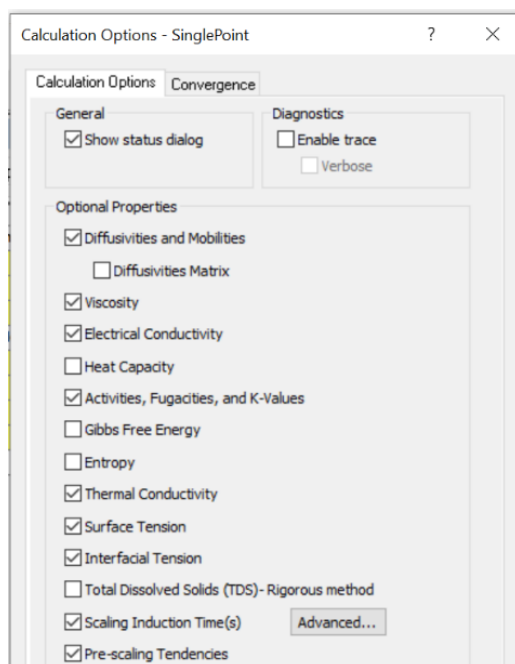


Figure 0-2 - Calculation Options window showing the Scaling Induction Time(s) check box

Example #1 – Induction times for CaCO_3 , BaSO_4 , and SrSO_4 in a Stream

The following stream contains low concentrations of CaCO_3 , BaSO_4 , and SrSO_4 in a NaCl brine at 25°C. We will use a few single point, isothermal calculations to show how the model works.

Step #1 – Create a basic induction time calculation

Add a stream and label it Basic Calculation (MSE model)

Add the four inflows and mole amounts: CaCO_3 – 0.001; BaSO_4 – 0.00005; SrSO_4 – 0.008; and NaCl – 0.1.

Basic Calculation		
Description		
Variable	Value	
Stream Parameters		
Stream Amount (mol)	55.6173	
Temperature (°C)	25.0000	
Pressure (atm)	1.00000	
Inflows (mol)		
H2O	55.5082	
CaCO3	1.00000e-3	
BaSO4	5.00000e-5	
SrSO4	8.00000e-3	
NaCl	0.100000	

Figure 0-3 - New Stream containing low concentrations of CaCO₃, BaSO₄, and SrSO₄ in a 0.1 NaCl electrolyte solution.

Add a single point calculation and label it *No Inhibitor*

When the calculation is complete, click on the **Report** tab. Then click on the **Customize** button in the upper right of the screen.

Deselect all boxes and then check the **Scaling Induction Time** box only

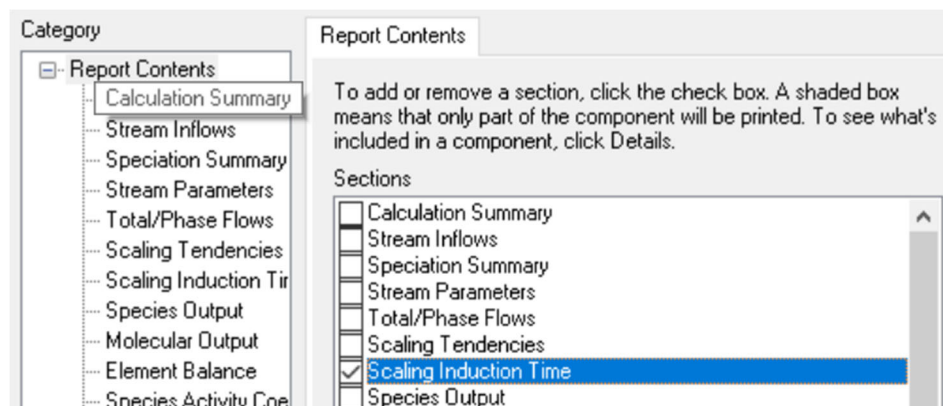


Figure 0-4 - The Report's Customize popup window showing where the Scaling Induction Time category is located

Review the column data in the Scale Induction Time(s) table

Scaling Induction Time(s)

	Induction Time	Scaling	Scaling
Solids	min	Tendency	Index
CaSO ₄ .2H ₂ O (Gypsum)	n/a	0.0256792	-1.59042
CaCO ₃ (Calcite)	8.66935	12.8217	1.10795
SrSO ₄ (Celestine (celestite))	7.02197	20.9219	1.32060
BaSO ₄ (Barite)	0.397590	275.421	2.44000

The three solid phases are supersaturated as shown in the Scaling Tendency column, and their induction times vary from 0.4 to 8.7 minutes. This means that barite will form in about 25 seconds while the other solids will take several minutes longer before they start to precipitate.

Step #2 – Adding scale inhibitors

Add a new single point calculation and label it *With Inhibitor*

You may have noticed already that there are + boxes to the left of CaCO₃, BaSO₄ and SrSO₄. These boxes expose a sub grid containing the available scale inhibitors for that specific mineral

Click on the + sign adjacent to BaSO₄ to expose the sub grid.

Click on the <select to add> box and select the NTMP – C₃H₁₂NO₉P₃ inhibitor. It will now appear at the bottom of the grid

<input type="checkbox"/> BaSO ₄	5.00000e-5
Available Inhibitors	<select to add>
<input type="checkbox"/> SrSO ₄	8.00000e-3
NaCl	0.100000
<input checked="" type="checkbox"/> C ₃ H ₁₂ NO ₉ P ₃	2.00000e-4

Give it an amount of 2e-4 moles (this is about 60 mg/l) and calculate

Click on the **Report** tab and once again, turn on only the **Induction Time** table using the **Customize** window

Scaling Induction Time(s)

	Induction Time	Scaling	Scaling
Solids	min	Tendency	Index
CaSO ₄ .2H ₂ O (Gypsum)	n/a	0.0256380	-1.59112
CaCO ₃ (Calcite)	n/a	0.159813	-0.796387
BaSO ₄ (Barite)	1692.73	279.068	2.44571
SrSO ₄ (Celestine (celestite))	7.28424	20.7554	1.31713

The induction time for BaSO₄ increased to 1692 minutes, a time that would likely prevent the solid from precipitating in the process. The calcite induction time now shows n/a, which means that the compute time exceeds the maximum limit of 10,000 hours. Only the SrSO₄ induction time remained the same.

Return to the Definition tab and select the + adjacent to SrSO₄. Select the HEDP – C₂H₈O₇P₂ inhibitor and give it a value of 2e-4 (~41 mg/l).

<input type="checkbox"/> BaSO ₄	5.00000e-5
Available Inhibitors	<select to add>
<input checked="" type="checkbox"/> SrSO ₄	8.00000e-3
NaCl	0.100000
<input type="checkbox"/> C ₃ H ₁₂ NO ₉ P ₃	2.00000e-4
<input type="checkbox"/> C ₂ H ₈ O ₇ P ₂	2.00000e-4

Re-calculate and view the Report table

Scaling Induction Time(s)

	Induction Time	Scaling	Scaling
<i>Solids</i>	min	Tendency	Index
CaSO ₄ .2H ₂ O (Gypsum)	n/a	0.0266380	-1.57450
CaCO ₃ (Calcite)	n/a	5.11185e-3	-2.29142
BaSO ₄ (Barite)	n/a	278.957	2.44554
SrSO ₄ (Celestine (celestite))	140.909	20.7065	1.31611

The SrSO₄ induction time has increased to 141 minutes and both barite and calcite no longer have values (n/a). The HEDP inhibited both SrSO₄ and BaSO₄. At these concentrations, the water would now be considered inhibited (and possibly overdosed!).

Step #3 – Using a concentration survey to compute the best inhibitor concentration

In the previous steps you created a supersaturated solution and then reduced its propensity to precipitate by adding a scale inhibitor. The inhibitor concentrations used were not optimized. You will use the survey calculation to vary the inhibitor concentration and find a reasonable value.

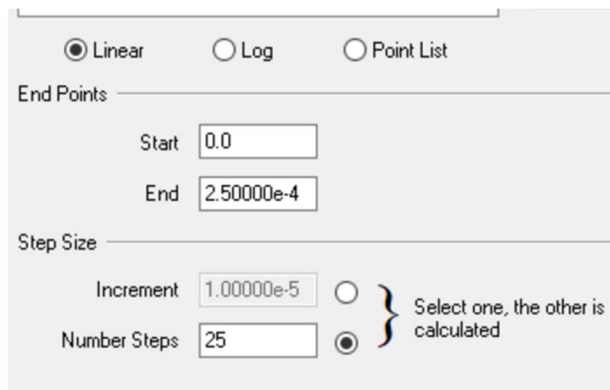
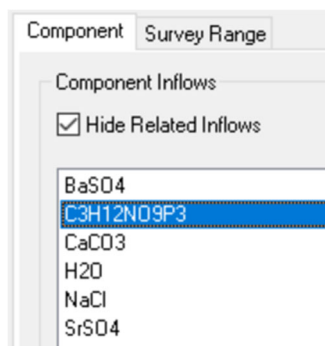
Add a **Survey** calculation and label it *Inhibitor survey*

Expand the BaSO₄ box and select NTMP - C₃H₁₂NO₉P₃ again

Change the Survey by from Temperature to Composition

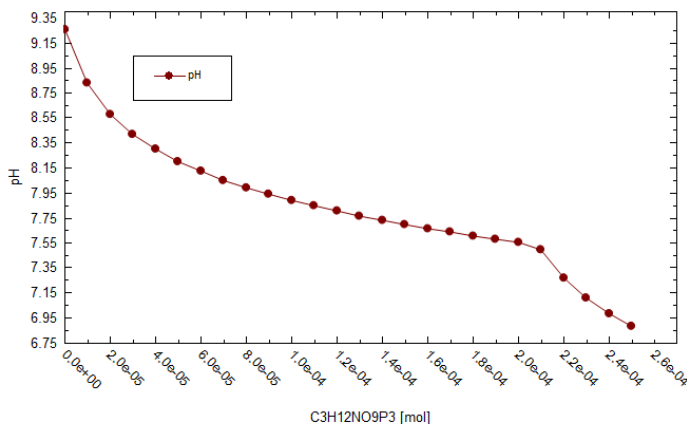
Open the **Specs** window, select NTMP as the component

Set the concentration range to start at 0, end at 2.5e-4, and have 25 steps



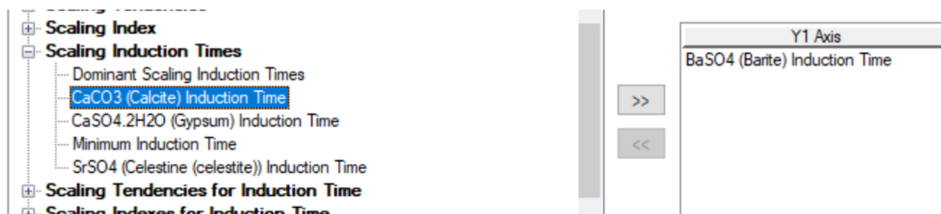
Calculate and select the **Plot** tab

The scale inhibitor has a significant impact on the pH because NTMP is a hexavalent acid. This will affect scale tendencies for carbonate solids if added in this way. Right now, we are looking at BaSO₄, and so we will ignore the impact on calcite



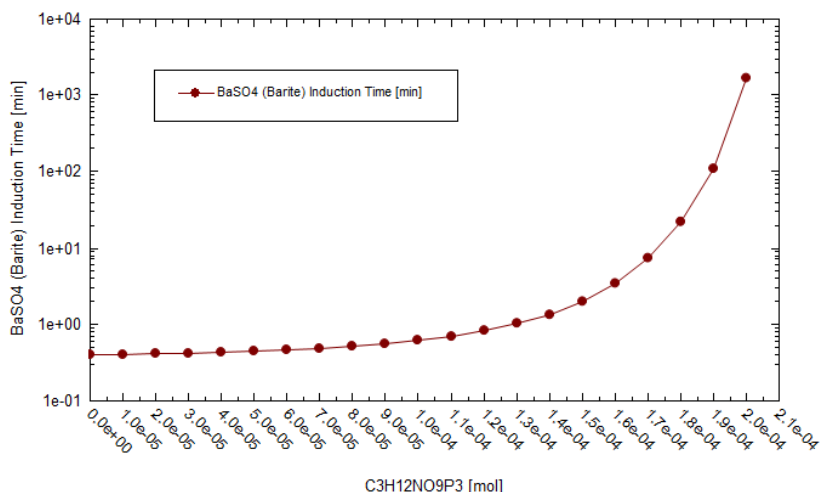
Click the **Variables** button to open the **Curves** window

Remove the pH from the Y1 axis and add the BaSO₄ induction time from the **Scaling Induction Times** category



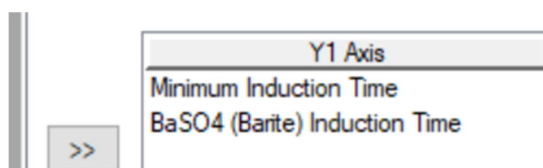
Set the y-axis to log scale

The plot now shows the barite induction times as the inhibitor is added. The induction times increase from 1 minute to 1692 minutes when the concentration increases from 1.3e-4 to 2.0e-4 moles (52 to 80 mg/L). Somewhere in this range would be the optimal inhibitor concentration.

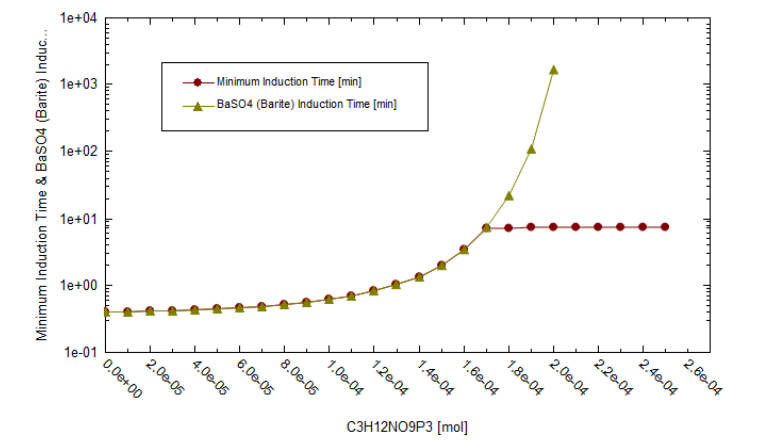


You will notice that the plot does not extend to the final concentration of 2.5×10^{-4} NTMP. It is because at this point the induction time exceeded the 10,000 hr maximum value.

Add the **Minimum Induction Time** variable (located under the **Scaling Induction Times** category) to the plot



This new plot offers a different perspective to the user's interpretation. You can now see that the two curves diverge at 1.8×10^{-4} moles. Because this inhibitor concentration barite is the solid phase that is the fastest to precipitate. As more inhibitor is added, barites induction time increases and eventually becomes greater than the next solid that forms, which in this case is SrSO_4 . So, the software is computing that below 1.8×10^{-4} moles inhibitor, barite will be the first solid to form. Above this concentration SrSO_4 is the first solid to form. This would also mean that a second scale inhibitor should be added to keep SrSO_4 from nucleating.



Step #4 - Using a temperature survey to test induction times

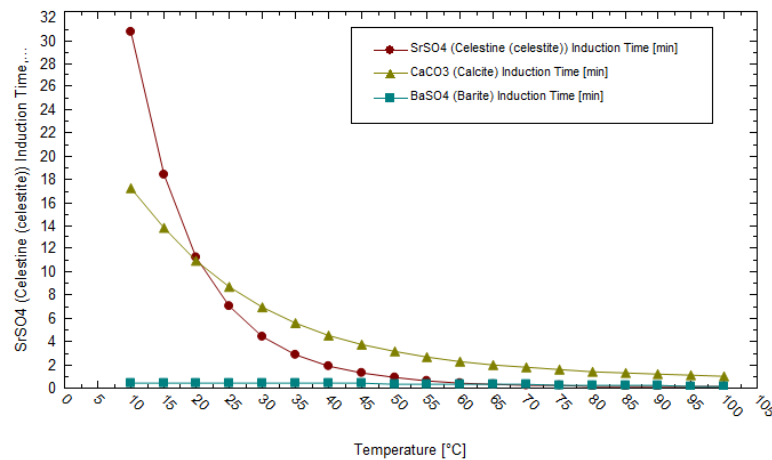
Induction times depend on both the scaling tendency of the solid (driving force for precipitation) and the temperature (reaction rates). Therefore, changes to either will result in different induction times for the solid.

Add a new **Survey** calculation and label it t_{ind} vs T

Set the temperature range from 10 to 100 °C by 5 °C increments, click **OK** and then **calculate**

Select the **Plot** tab and plot the induction times for the three solids, CaCO₃, BaSO₄, and SrSO₄

The plot shows how temperature affects induction times. At 10 °C, CaCO₃ and SrCO₃ induction times are at 18 and 31 minutes, respectively. At 100 °C, the induction times for the 3 of them are less than 1 minute.



Example #2 – Using induction times in a Mixer calculation

A common cause of scaling is when two incompatible streams are mixed together. For example, one stream containing a high calcium concentration and the other containing high concentrations of carbonate. The software will compute the induction times during the time of mixing using the Mixer block. This next example shows this.

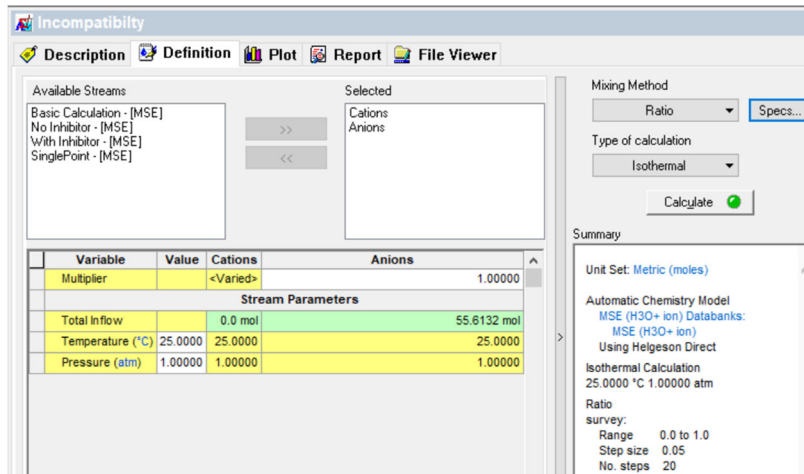
- 1) Add a stream and label it *Cations*
- 2) Add CaCl₂ and NaCl to the grid. Set the values to 0.005 and 0.1 moles, respectively

Inflows (mol)	
H2O	55.5082
CaCl2	5.00000e-3
NaCl	0.100000

- 3) Add a second stream and label it *Anions*
- 4) Add Na₂CO₃ and NaCl to the grid. Set the values at 0.005 and 0.1 moles, respectively

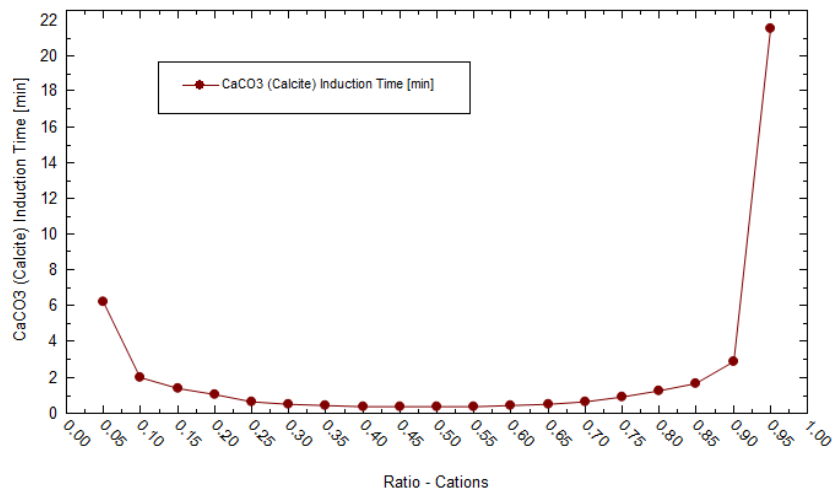
Inflows (mol)	
H2O	55.5082
Na2CO3	5.00000e-3
NaCl	0.100000

- 5) Add a Mixer calculation and label it *Incompatibility*
- 6) Move the Cations and Anions streams to the **Selected** Section
- 7) Set the **Mixing Method** to **Ratio**
- 8) Open the **Specs** window and select Cations as the Ratio stream.
- 9) Under the **Survey Range** tab set the steps to 20



- 10) **Calculate** and go to the **Plot** tab
- 11) Plot the CaCO₃ induction times

The plot shows that induction times are lowest (fastest to form) at a 50:50 mixture and highest at the far ends of the plot. In fact, at the 0 and 100% points, no induction times are shown because there is no calcium in the 0% calculation and no carbonate in the 100% calculation.

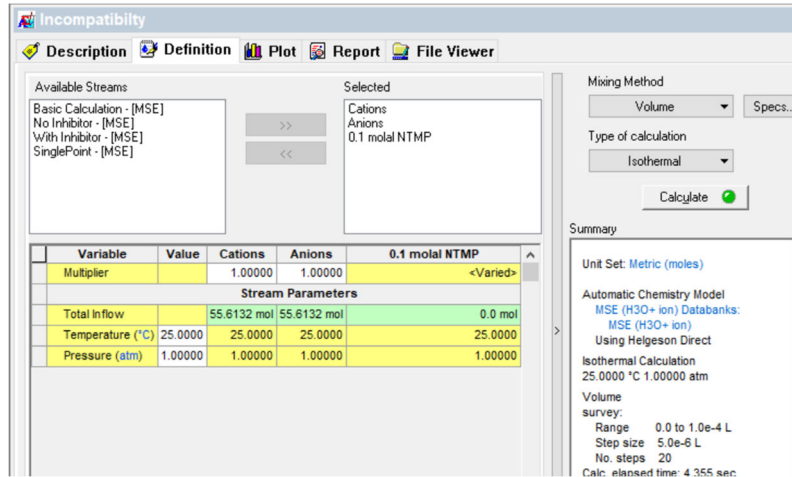


Scale inhibitors can also work in the mixer calculation but to do this, the user must create a separate stream and add it to the mixer like it would occur in a process.

- 12) Create a new stream and label it 0.1 molal NTMP

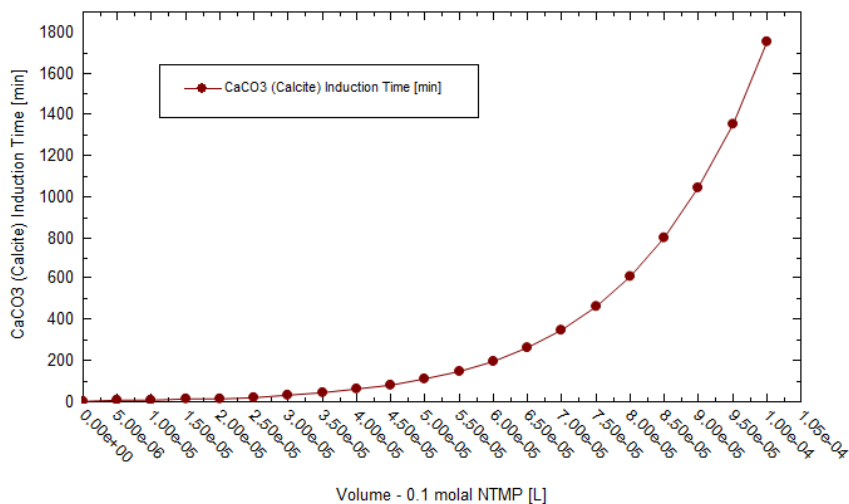
Again, we are disregarding practical units in this example so that we can focus on the procedure of studying induction times.

- 13) Add NTMP to the grid and give it a value of 0.1 mole
- 14) Return to the Incompatibility mixer and add the 0.1 molal NTMP stream to the Selected window
- 15) Change the mixing type from Ratio to Volume
- 16) Open the **Specs** window and select the 0.1 molal NTMP as the adjustable stream
- 17) Set the start and end to 0 L and 1e-4 L, respectively. Set the steps to 20.



- 18) **Run** the calculation and click on the **Plot** tab when done
- 19) Add the CaCO₃ induction time to the plot and click OK

As NTMP is added to the mixture, the calcite induction time increases from less than one minute to over 1600 minutes. Somewhere in this addition would be the optimal treatment value, and that would depend on how long the solid needs to remain in solution. For example, 200 minutes is over three hours, a time that would probably be enough for a fluid to exit any process unit, like an RO or mixing tank. This would correlate with a 6e-5 L or 0.060 mL dosage per the two liters of mixed material.




An alternative way to plot this would be to use the MBG-Liquid 1 variables. Instead of plotting the volume of the NTMP added, you can plot the concentration of NTMP in solution. This concentration would be the minimum inhibitor concentration desired, or perhaps the residual concentration that you want to keep in solution.

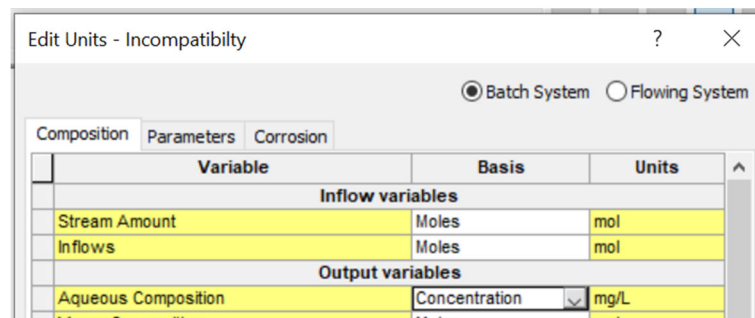
20) Open the **Variables** button and expand the MBG Totals - Liquid 1 category

21) Move NTMP(-6) to the X-axis



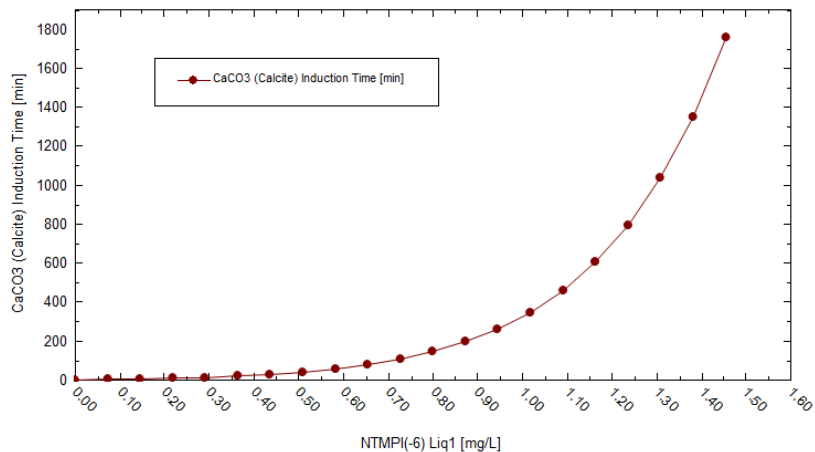
22) Close the **Variables** window and open the Units Manager ()

23) Click on the **Customize** button and change the *Aqueous Composition* from moles to Concentration



24) Close the units manager and review the plot

According to the calculation, a residual NTMP concentration of about 0.6 mg/l will keep CaCO₃ from precipitating for 60 minutes. A concentration of 1 mg/L will inhibit precipitation for about 6 hours (348 minutes).



More Induction time options

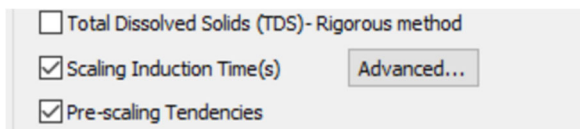
The induction time calculation is a post-process calculation, meaning that it calculates the scale tendencies and t_{ind} after the system converges to equilibrium. This means that the software will keep the target solids in solution

so that it can calculate its supersaturation. Competing solids that remove precipitating ions from the water can impact the induction times. For example, BaSO_4 is supersaturated, but CaSO_4 also precipitates, and in doing so, removes sulfate from solution. This sulfate removal affects the final BaSO_4 induction time. The software must be able to accommodate conditions where such mass actions impact the calculation. It does this in the **Calculation Options** window.

Click on any of the calculations you created using this chapter

Select the **Specs** button and then the **Calculation Options** tab (or category)

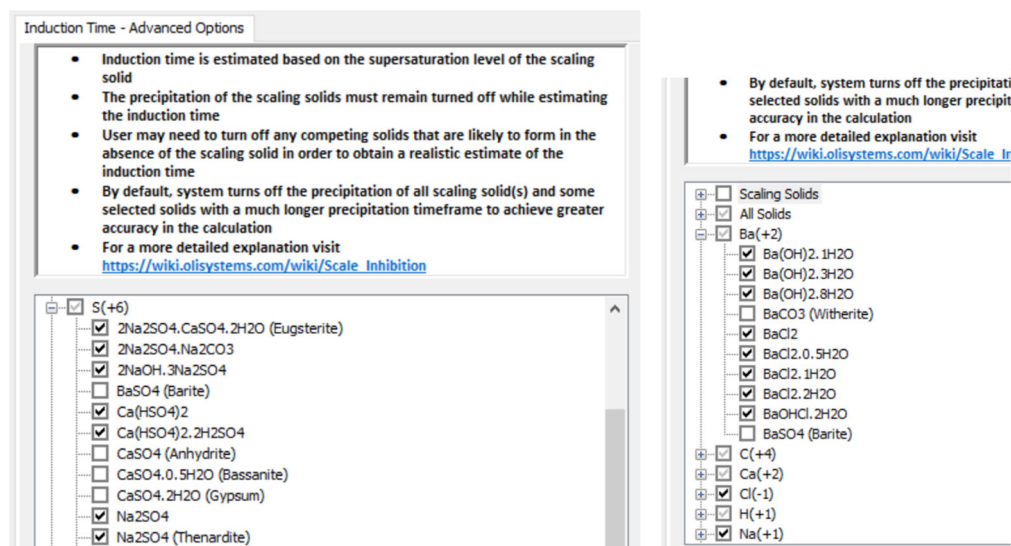
Click on the Advanced button adjacent to the Scaling Induction Times(s) check box



Expand the S(+6) category in the window

The text in the upper section of the window explains how the induction times work. It explains that the induction times are based on the supersaturation level of the specific solid and that for this solid to be supersaturated, it must not precipitate during the induction time calculation. In addition to the target solid, any competing solids that might change the concentration in the supersaturation equation (Ba and SO_4 if the calculation is for BaSO_4) also needs to be turned off. Otherwise, the supersaturation of the target solid will be lowered and a less accurate induction time value will be computed.

So, in this case, potential competing solids for BaSO_4 include three CaSO_4 phases and BaCO_3 . These are turned off by default. There are many other Ba- and SO_4 -containing solids that can form, and if you see them forming in your induction time calculation, you can go to this window and turn them all off.



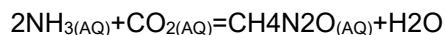
You may also decide that these competing solid should affect the induction time of your target solid. In that case, you turn those solids on. When that happens, reduced concentration of the target solid's ions will be used to compute the induction time.

Chapter VII – Naming Conventions in OLI Studio and Definitions

OLI naming conventions are important to understand as they become critical in performing advanced features in OLI Studio. The following chapter explains OLI naming conventions, when they're important, and provides key definitions for understanding these conventions.

Naming the Phases of Species

Let's say for example you want to type the following reaction in the OLI reaction kinetics tool:



Note: You must use the **OLI Tag Name** for this step, and additionally specify the phase of the reactants and products. Water is a special case; it is written only as H2O.

As a general rule:

For an aqueous phase: AQ

For a vapor/gas phase: VAP

For a solid phase: PPT

For a hydrated solid: SOLIDNAME.nH2O, where n is the hydration number

For an ion: ION

You can find the OLI TAG Name of your specific species using the [Component Search Tool](#).

In OLI terminology the above reaction will look like:



Ionic Strength

Ionic Strength (molal based or m-based)

The ionic strength is a quantity representing the strength of the electric field in a solution, and it is equal to the sum of the molalities of each type of ion present multiplied by the square of their charges, as represented by the following equation:

$$I = \frac{1}{2} \sum_{i=1}^n (z_i^2 m_i)$$

Where n is the number of charged species

For example, a 1.0 molar solution of NaCl has 1.0 moles of Na^+ ions and 1.0 moles of Cl^- ions in 1 kg of H_2O . Therefore, the ionic strength is 1.0 molal.

$$I = \frac{1}{2} ((z_{\text{Na}^+})^2 (m_{\text{Na}^+}) + (z_{\text{Cl}^-})^2 (m_{\text{Cl}^-}))$$

$$I = \frac{1}{2}((1)^2(1) + (-1)^2(1)) = 1$$

Now, consider a 1.0 molal solution of CaCl_2 . This solution has 1.0 mole of Ca^{+2} ions and 2.0 moles of Cl^- ions in 1 kg of H_2O . Therefore, the ionic strength is 3.0 molar, or it can be said that a 1.0 molal solution of CaCl_2 behaves similar to a 3.0 molar solution of NaCl .

$$I = \frac{1}{2}((z_{\text{Ca}^{+2}})^2(m_{\text{Ca}^{+2}}) + (z_{\text{Cl}^-})^2(m_{\text{Cl}^-}))$$

$$I = \frac{1}{2}((2)^2(1) + (-1)^2(2)) = 3$$

Ionic Strength (mole fraction based or x-based)

In this case the ionic strength is calculated using the mole fraction rather than the molality:

$$I = \frac{1}{2} \sum_{i=1}^n (z_i^2 x_i)$$

Where n is the number of charged species.

Material Balance Group (MBG)

MBG is an abbreviation for Material Balance Groups. The **MBG** variable is a sum of all the species with the same oxidation state. OLI gives this information as Total or for the specific phase requested (Aqueous, Vapor, Solid, and Organic) or as absorbed to the surface.

For example, if we have the following system:

55.5082 moles of H_2O

1 mol of NaCl

1 mol of CaCl_2

1 mol of CaCO_3

The distribution of the elements with their respective oxidation states are given as MBG for the total system, and for the phases that are predicted to form, as shown in the image below.

Description Definition Report

Variable	Value
Stream Parameters	
Stream Amount (mol)	58.5082
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Inflows (mol)	
H2O	55.5082
NaCl	1.00000
CaCl2	1.00000
CaCO3	1.00000
MBG Totals - Totals (mol)	
H(+1)	111.016
Na(+1)	1.00000
Ca(+2)	2.00000
O(-2)	58.5082
Cl(-1)	3.00000
C(+4)	1.00000
MBG Totals - Aqueous (mol)	
H(+1)	111.016
O(-2)	55.5083
Cl(-1)	3.00000
Ca(+2)	1.00002
Na(+1)	1.00000
C(+4)	1.97427e-5
MBG Totals - Solid (mol)	
O(-2)	2.99994
C(+4)	0.999980
Ca(+2)	0.999980

Type of calculation: Isothermal

Summary

Unit Set: Metric (moles)

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

Isothermal Calculation
 25.0000 °C 1.00000 atm

Phase Amounts
 Aqueous 60.5083 mol
 Vapor 0.0 mol
 Solid 0.999980 mol

Aqueous Phase Properties
 pH 8.02574
 Ionic Strength 0.0661064 mol/mol
 Density 1.11694 g/ml

Calc. elapsed time: 1.291 sec
 Calculation complete

Volume vs. Volume at Standard Conditions vs. Standard Liquid Volume

Volume

This is the volume of the system at a specified temperature, pressure, and composition.

Volume at Standard Conditions

It is also known as the Standard Volume. This is the calculated volume of each phase (using the composition of each phase) at standard conditions. The standard conditions for each phase: vapor, liquid-1, and liquid-2 are predefined in the software, and can be changed.

The standards conditions are:

Vapor: Temperature: 15°C and Pressure: 1.0023 atm

Liquid-1: Temperature: 25°C and Pressure: 1 atm

Liquid-2: Temperature: 15°C and Pressure: 1 atm

Standard Liquid Volume

This is a transport unit. Standard liquid volume is the calculated standard liquid volume based on true species. You can see it as the contribution of volume of each true species to the total liquid volume.

An example

Standard liquid volume calculation of Liquid-1 phase (MSE), H₂O: 55.5082 mole, NaCl: 1 mole, 25°C, 1 atm (using OLI Studio 9.5.4).

Standard liquid volume of material balance group (MBG) (accessible through Databank > literature >Material codes > VOLU).

MBG name	Standard liquid volume of MBG, VOLU (m ³)
H(+1)	1.41E-05
Na(+1)	1.82E-05
O(-2)	-1.02E-05
Cl(-1)	1.72E-05

True species composition after speciation:

True species (Name)	Composition (COMP), mole
H ₂ O	55.5082
Cl-1	1
Na+1	1
H ₃ O+1	1.33E-07
OH-1	1.33E-07
NaOH	5.30E-14
HCl	2.07E-15

Standard liquid volume of the phase calculation, considering MBG group contribution in each true species:

MBG Name	Contribution	Contribution Value
H(+1)	$1.41E-05 \times (55.5082 \times 2 + 1.33E-07 \times 3 + 1.33E-07 \times 1 + 5.30E-14 \times 1 + 2.07E-15 \times 1)$	1.57E-03
Na(+1)	$1.82E-05 \times (1 \times 1 + 5.30E-14 \times 1)$	1.82E-05
O(-2)	$-1.02E-05 \times (55.5082 \times 1 + 1.33E-07 \times 1 + 1.33E-07 \times 1 + 5.30E-14 \times 1)$	-5.65E-04
Cl(-1)	$1.72E-05 \times (1 \times 1 + 2.07E-15 \times 1)$	1.72E-05
	Volume (m ³)	0.00103827
	Volume (L)	1.03827

Index

Adiabatic, 219, 226
 Alloy Chemistry, 321
 API Gravity, 396
 Aragonite, 61
 Assay, 394, 395
 ASTM, 393
 ASTM D1160, 393
 ASTM D2887, 393
 Brines, 403, 427, 429, 436, 437, 438
 Calcium Carbonate, 61
 Calculation Types, 322
 Cascading Mixers, 225
 Cavett, 206, 395
 Composition Survey, 222, 338
 Contour Plot, 163, 167
 Corrosion, 260, 266, 272, 330, 346, 361
 density, 206, 396, 397, 419
 Depletion Parameters, 321
 Depletion Profile, 322, 335
 Dew Point, 48
 Dolomite, 70
 Electroneutrality, 195, 381, 419
 Equation of State, 17
 Equilibrium Constant, 111, 114
 Extreme Value Statistics
 EVS, 345, 346
 Gases, 403, 427, 438
 hydrocarbon, 424
 Isothermal, 38, 228
Lee-Kesler, 395
Mixed Solvent Electrolyte
 MSE, 16, 17
 Mixer, 225, 226, 228, 230, 427
 Oxidation, 252, 256, 257, 259
 Passivation, 262, 266, 267, 272
pH, 34, 38, 58, 121, 122, 123, 130, 133, 134, 135, 138,
 139, 222, 223, 224, 227, 229, 230, 236, 259, 262, 269,
 271, 274, 276, 278, 397, 419, 436, 437
 Pit Depth, 345, 346, 369
 Pressure Survey, 143, 163
 Pseudo-components, 395
 Reaction Kinetics, 101
 Redox, 256
 Reduction, 244, 252, 259, 274, 276
 Scaling Tendency, 180
 Selective Redox, 256
 Soave Redlich Kwong
 SRK, 17
 Speciation, 134, 220
 Stability Diagram, 263
 Temperature Survey, 123
 Thermal Aging Temperature Survey, 322
 Thermal Aging Time Survey, 322
 Thermodynamic Framework, 114, 225
 Tree View, 122, 134

True Boiling Point

Watson K, 394, 395, 397

TBP, 393