

# OLI Studio: ScaleChem Basics

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think simulation

getting the chemistry right

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

- OLI Systems Support Email: <u>oli.support@olisystems.com</u>
- Product Downloads: <u>http://downloads.olisystems.com/</u>
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### Disclaimer

This manual was produced using the OLI Studio / OLI Analyzer 10.1 build 1 (10.1.1). As time progresses, new data and refinements to existing data sets can result in values that you obtain being slightly different than what is presented in this manual. This is a natural progress and cannot be avoided. When large systematic changes to the software occur, this manual will be updated.

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## Chapter 1 – Introduction to OLI Studio: ScaleChem

## **About This Manual**

This manual uses **OLI Studio: ScaleChem** to model real world scaling situations while learning scaling theory and science, and the reasoning for making certain decisions with the software. Explanations of theory, science, software decisions, and ScaleChem features appear in plain text. Checkmarks ( $\checkmark$ ) accompany systematic tasks. Sidebars and remarks are shaded.

In Chapters 2-5, we model a hypothetical field and learn about basic ScaleChem tools. We model a new field in Chapter 6 then combine the two fields together in Chapter 7. Chapters 8-11 use real world field examples. Chapters 20 discusses Alkalinity calculations.

If you have not yet installed the software, please install it following the instructions given in Installation and Security page in our Wikipage at: <a href="http://wiki.olisystems.com/wiki/Installation\_and\_security">http://wiki.olisystems.com/wiki/Installation\_and\_security</a>.

### **OLI Studio Components**

The OLI Studio is a software suite containing several modules including, Stream Analyzer, ScaleChem and Corrosion Analyzer. A client's license determines which modules are enabled within the OLI Studio Software.

### Stream Analyzer

Stream Analyzer is standalone software, and it is the main interface of the OLI Studio. Stream Analyzer is a comprehensive thermodynamic tool that calculates speciation, phase equilibria, enthalpies, heat capacities and densities in mixed-solvent, multicomponent systems. Capabilities and features of Stream Analyzer are:

- Three different thermodynamic frameworks:
  - o Aqueous (AQ) model
  - o Mixed Solvent Electrolyte (MSE) model
  - Mixed Solvent Electrolyte and Soave-Redlich-Kwong (MSE-SRK) model

- Thermophysical properties: Stream Analyzer has thermophysical models to predict surface tension, interfacial tension, viscosity, electrical conductivity, thermal conductivity, diffusivity, and osmotic pressure.
- Molecular and ionic inflows: Stream Analyzer accepts molecular inflows, typical of a process stream, and ion inflows, typical of a sample water analysis.

## ScaleChem

ScaleChem is a simulation software tool that predicts scaling problems during oil and gas production. ScaleChem simulates fluid production from the reservoir to the sales point, and computes the phase mass balance, scale tendencies, and scale mass of production fluid at each location in the production line. Capabilities and features of ScaleChem are:

- Brine, gas and oil analysis
- Scaling scenarios
- Compatibility testing of brines using the stream mixing function
- Phase equilibrium calculation used to perform four-phase reservoir saturation, from which as whole fluid reservoir composition is determined
- Contour plots to study produced brine properties across a broad temperature and pressure range

### **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. It is used to predict the corrosion rates of general corrosion, propensity of alloys to undergo localized corrosion, depletion profiles of heat-treated alloys, and thermodynamic stability of metals and alloys. It enables users to address the causes of aqueous corrosion by identifying its mechanistic reasons. As a result, users take informed action on how to mitigate or eliminate this risk.

Corrosion Analyzer calculates corrosion by quantifying the bulk chemistry, transport phenomena, and surface reactions through a thermophysical and electrochemical module.

The thermophysical module calculates the aqueous solution speciation and obtains concentrations, activities and transport properties of the reacting species.

• The electrochemical module simulates partial oxidation and reduction process on the metal surface.

The tool reproduces the active-to-passive transition and the effects of solution species on passivity.

Effects of temperatures, pressure, pH, concentration, and velocity on corrosion are also included. Capabilities and features of Corrosion Analyzer are:

- Generation of Pourbaix (E vs pH) diagrams
- Calculation of general corrosion rates
- Localized corrosion susceptibility
- Heat treatment effect
- Generation of polarization curves plots

### What is OLI Studio: ScaleChem?

OLI Systems, Inc. is an electrolyte-thermodynamics research company. The OLI Studio is its flagship software suite. When we open the OLI Studio, a splash screen indicates the available subsets or modules that our license enables. These subsets include Stream Analyzer, Corrosion Analyzer, and Studio ScaleChem. The modules all share a common interface.



We use the phrase Studio ScaleChem (SSC) to distinguish it from the original ScaleChem or ScaleChem Standard. ScaleChem Standard predicted the four-phase chemistry of produced fluids. The software covered the chemistry specific to oil and gas production and their respective mineral phases. In 2012-2013, OLI product developers incorporated ScaleChem technology into the OLI Studio.

The Shell Oil Company originally developed the technique to predict high temperature and pressure effects on brines. In the 1980s, OLI linked this technique to its own predictive aqueous model. In the 1990s, OLI replaced this model with a rigorous temperature and pressure model, the Helgeson-Kirkham-Flowers Equation of State. OLI refit all accepted mineral scaling experimental data to the new model. The model has been the industry mainstay ever since and is considered the standard for such calculations.

## Why Use Studio ScaleChem?

Scale problems arise when fluid, initially in equilibrium with its environment, is disturbed and becomes unstable. The unstable fluid results in  $H_2O$ ,  $CO_2$ , and  $H_2S$  partitioning across the water, oil, and gas phases, corrosion of metal surfaces, and precipitation/dissolution of solids. SSC 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. SSC 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.

### General View of the OLI Studio User Interface

In the OLI Studio Software, the OLI Studio Desktop User Interface provides the environment to create, analyze and interpret the results of your application chemistry. In this manual, an overview of the different windows and tools that you will be using within the software, as well as how to navigate the OLI Studio User Interface, will be provided here.

The initial screen shows several panes or boxes, some of which we can minimize, pin, and move using the corner icons or by selecting View > Toolbars from the Menu Bar. Most of the screenshots used in this manual will not show the Object Library, Plot Template Manager, and Calculation Output Pane

0 O	OLI Studio - [Document1] File Edit Streams Calculations Ch	emistry Tools View Window Help Menu Bar	- 🗆 X	
Navigator Panel	File Edit Streams Calculations Ch The Control of the Control of t	emistry Tools View Window Help Menu Bar L1 Va So L2 Re 2 Wet 2 We		Object Library
Actions Panel Action Action Plot Template Manager	ns + × ins	Automatic Chemistry Model Aqueous (H+ Ion) Databanks: Aqueous (H+ Ion) Using K-ft Polynomials T-span: 25.0 - 225.0 P-span: 1.0 - 1500.0	Moist Air (50% hu Components Sea Water Sea Water Standard Seawat Water Standard Standard	
Catedration Output + X	eln press F1	Calculation Output Panel		

The screenshot shown above is what you will see when you first start OLI Studio. You can customize the desktop to your own needs. The windows can be resized, moved, docked and detached.

#### Panels Relevant to OLI Studio: ScaleChem

The most important panes are described below. The training manual or instructor will provide further details about components of each pane. More information is also available by selecting **Help > Help Topics** from the menu bar, or by contacting OLI technical support.

#### Navigator

This pane contains the icons and names of each action in a hierarchical tree. This pane displays active Analyses (*Brine, Gas, and Oil*) and Calculation (*Scale Scenario, Saturators,* etc.) objects. OLI refers to Analysis and Calculation objects as *Streams*, which we "add" to the Navigator.



Navigator View with SSC objects

*Filename* A star next to a filename indicates that the file has been modified but not yet saved

**Global Streams Level** Provides the broadest view of objects in the Navigator

Stream Level Where we enter chemistry

**Calculation Level** After completing calculations, the software automatically adds daughter or sub-streams. We can view sub-streams by clicking the "+" sign to the left of the parent stream, as shown below

### Actions

The Actions Pane shows all objects that we can add to the *Navigator*. The objects shown in this pane are available depending on a client's license.



Actions Pane (shown in large icon view with widened window)

The *Actions* pane is contextual and changes depending on the selected stream. We can add objects by double-clicking the Actions Pane icon or through the Menu bar using Streams > ScaleChem or Calculations > ScaleChem.

		C <u>a</u> lculations <u>C</u> hemistry <u>T</u> ools <u>\</u>	<u>/</u> iew <u>W</u> indow <u>H</u> elp
		Single Point	
Streams Calculations Chem	istry <u>T</u> ools <u>V</u> iew <u>W</u> ine	Surveys	👌 🛨 MSE 🛨 🖓 🛨 👫 🛤
Add Stream	Cancel	Add Mixer	
Add New Analysis	q Va So 2 <sup>nd</sup> Re 🛓	Add Reconciliation	反 Report 🔛 File View
ScaleChem 🕨	Add Oil	Rates of Corrosion	•
🥌 Descri	Add Gas	ElectroChemical Diagrams	Value Balanced     ons (mg/L)
	Add Brine	ScaleChem	Add Scenario
	Variable	Potassium ion(+1)	Add Saturator

Add objects by selecting the icon in the Actions pane or through the Menu bar

### Description

This pane contains the *Design, Report, Description* and other tabs. This pane changes depending on the active object. When we add any SSC object, the screen automatically switches to the *Design* tab, which is unique for each object. Each *Design* tab has a set of colored vertical tabs with data entry screens. Most objects also have a Summary box and certain Calculation objects display a *Plot* tab.

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	Na+1	0.0	0.0	s						ø		Component	Value	Normalized	
Dat	K+1	0.0	0.0	tion						Š	Г	•	Subtot	Subtotal:	
	Ca+2	0.0	0.0	ipu						E		H2O	0.0	0.0	
	Mg+2	0.0	0.0	Ŭ								N2	0.0	0.0	
cile	Sr+2	0.0	0.0									CO2	0.0	0.0	
Co	Ba+2	0.0	0.0	Pilo	D	etail Info of				jo j		H2S	0.0	0.0	
å	Fe+2	0.0	0.0	ŭ	Г	Compor	ent	Value		COL		CH4	0.0	0.0	
						-				Ř					

Description Panes of ScaleChem objects. Brine Analysis (left), Scale Scenario (middle), and Gas Analysis (right).

## Chapter 2 – Olympus Brine Analysis & Scale Scenario

## **Overview**

This chapter focuses on two **ScaleChem** objects, *Brine Analysis* and *Scale Scenario*. You will input a water analysis and its measured properties into a *Brine Analysis* object. This is Task 1. You will then test the brine properties in a *Scale Scenario* object to compute if the mineral scales will precipitate as the fluid flows up the well. This is Task 2.

### Setting up the Work File

✓ Launch the software

or 🌔	l Studio - [Document1]		-	
E Fil	e Edit Streams Calculations Chemistry	Tools V	iew Window Help	_ 8 ×
i c	New	Ctrl+N	ke ± 🗛 ± 🗱 ± 🗛 ± 🗄 🚧 🎬 ± 🛟 🔉 😭 🖉	
Nav	Open	Ctrl+O		
Do	Close			
-	Save	Ctrl+S		
	Save As		Date: 1 / 2 /2020	
	Import	>	Date: 17372020 V	
	Print	Ctrl+P		
	Print Preview			^
	Print Setup			
	Properties			

- ✓ Select File > Save As... from the menu bar
- ✓ Type SSC Basics or another title in the File name field, then click Save

File name:	SSC Basics		~
Save as type:	OLI Studio Files (*.oad)		~
ide Folders		Save	Cancel

A typical OLI Studio software installation creates a folder within a PC's Document directory called "My OLI Cases." By default, OLI Studio cases (files that end with the \*.oad extension) are stored in this folder.

## Task 0 – Set Thermodynamic Framework to MSESRK

Before starting the calculations, you will change some settings.

✓ Click on the **Streams** object in the Navigator Panel

SSC Basics	.oad
🍫 Streams	

 Change the name from Streams to ScaleChem Training by double clicking on it or changing the name directly in the Description tab

Navigator # * X SSC Basics.oad*	🔩 ScaleChem Training
ScaleChem Training	Description Object Map
	Name: ScaleChem Training

✓ Select Chemistry>Model Options from the Menu

Che	mistry	Tools	View	Wind
	>			
	>			
	Model	Option	s	
_	wode	Option	S	

✓ Change the Thermodynamic Framework to MSE-SRK (H3O+ ion)

Default Che	?	×	
Databanks	Redox Phases T/P Span		
Databan	ks Thermodynamic Framework		
	MSE-SRK (H3O+ ion) V		

## Task 1 – Create a New Brine Analysis

Your first action is to create the brine analysis object. You will use the data in the table given below.

✓ Add a Brine Analysis from the Actions panel by double clicking on it. Or select the Brine Analysis from the menu (Streams > ScaleChem > Add Brine)



Bright click on the Actions Panel to display the objects in the List format



The *Brine Analysis* opens to the *Design* tab and the *Data Entry* grid. Before inputting the brine's composition, you will perform a few formatting changes to make your work go smoother.

- ✓ Select the **Description** tab
- ✓ Change the brine name to *Olympus 1 Brine*

You can also highlight the icon in the Navigator and select the <F2> key to change object names.

Navigator # * *		uius e	
SSC Basics - Chapter 02.oad		rine	
🏘 ScaleChem Training	🦪 Description	🛃 Design	髮 Report
Olympus1 Brine			
	Name: Olympus1 B	Irine	

- ✓ Select the Design tab
- ✓ Click on the Display dropdown button and select Formula

Navigator 🛛 🗛 🔺 🗙 SSC Basics - Chapter 02.0ad*	😼 Olym	ipus1 Brine				
ScaleChem Training	🦪 Des	cription 🔮 Design <u> </u>	Report			
		Variable	Value	Balanced	Entry Options	
	L L	Cations (n	ng/L)		Units	
	a	Na+1	3600.00	3600.00	mal	
	Dat	K+1	300.000	300.000	Dieplay	
		Ca+2	600.000	600.000	Cispiay	
		Mg+2	150.000	150.000	Formula ~	
	e.	Sr+2	80.0000	80.0000	Eormula	
	co	Ba+2	5.00000	5.00000	OLI Tag	

✓ Enter the concentrations from the table below

	Table 1: Olympus 1 Brine Analysis									
Cations mg/L		Anions mg/L		Neutrals mg/L		Measured Properties				
Na+1	36000	CI-1	57000	SiO2	15	Temperature	25 ℃			
K+1	300	SO4-2	250			Pressure	1 atm			
Ca+2	600	HCO3-1	600			рН	7.67			
Mg+2	150					Alkalinity				
Sr+2	80					Density (g/ml)	1.064			
Ba+2	5					Total Dissolved Solids (mg/l)	96280			

✓ Make sure to select the **Dominant Ion** balance option type

The software balances charges according to the selected option and displays this in the yellow column. Notice in the *Data Entry* grid's *Balanced Column* (yellow column) that the Na+ concentration is 36,116 mg/l.

✓ Review the **Summary** panel. The **Dominant Ion Charge Balance** is summarized there.



The *Summary* box shows additional detail about the brine. The Stream Parameters table shows default values. The **Dominant Ion Charge Balance** shows the cations and anions equivalents and the charge imbalance. The charge imbalance is -0.005 eq and the software added 116 mg/L of Na<sup>+1</sup>.

The four available **Balance Options** are explained below.

<b>Dominant Ion.</b> The dominant ion of the deficient charge is added. The dominant ion is based on moles/kg concentrations.	
	Balance Options
<ul><li><i>Prorate Cation.</i> The complete set of cations is prorated (all concentrations are multiplied by the same ratio).</li><li><i>Prorate Anion.</i> The complete set of anions is prorated.</li></ul>	Type Dominant Ion Prorate Cation Prorate Anion Makeup Ion
<i>Makeup Ion.</i> The user selects an ion. Its concentration is then increased or decreased depending on the charge requirements.	

The next step is to enter measured properties and calculate the brine properties. This is done in the *Reconcile* tab.

- ✓ Select the **Reconcile** (blue vertical) tab
- ✓ Enter the measured pH (7.67), Density (1.064 g/ml), and TDS (96280 mg/L)

oncile Data Entry	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			Calculate 🥥	
0		Description		a second second	
~		Properties	IV	easured	Calculated
æ	F	Temperature (°C)	IV	25.0000	Calculated
Re	F	Temperature (°C) Pressure (atm)	IV	25.0000 1.00000	Calculated
Re		Temperature (°C) Pressure (atm) pH	IV	25.0000 1.00000 7.67000	Calculated
Re		Temperature (°C) Pressure (atm) pH Alkalinity (mg HCO3/L)		25.0000 1.00000 7.67000 600.000	Calculated
Re		Temperature (°C) Pressure (atm) pH Alkalinity (mg HCO3/L) Density (g/ml)		25.0000 1.00000 7.67000 600.000 1.06400	
Re		Temperature (°C) Pressure (atm) pH Alkalinity (mg HCO3/L) Density (g/ml) Elec Cond, specific (µmho/cm)		25.0000 1.00000 7.67000 600.000 1.06400 0.0	

The next step is to calculate the brine properties. There are five calculation, or Reconciliation, options that are described below.

- 1. **Concentration Data Only**. This approach uses ion concentration data only. The pH is computed from the concentration of weak acid and base ions (e.g., HCO<sub>3</sub><sup>-1</sup>, CO<sub>3</sub><sup>-2</sup>, HS<sup>-1</sup>, Acetate<sup>-1</sup>, and Fe<sup>+2</sup>), and of acids and bases (e.g., CO<sub>2</sub>, H<sub>2</sub>S, H<sub>3</sub>BO<sub>3</sub>, Acetic acid, even HCI). This is the default option.
- 2. Gas-Phase CO<sub>2</sub> Content (mole%). This option uses the concentration data described above plus the CO<sub>2</sub> partial pressure. For instance, air contains 400 ppmV (0.04 mol%) CO<sub>2</sub>. This 0.04 mole % is entered in the CO<sub>2</sub> fraction field, the pressure is set to 1 bar, and the software computes the properties of a brine that is in contact with air. Similarly, the software can compute the brine in a separator if that CO<sub>2</sub> and pressure are entered.
- 3. *Measured pH and Alkalinity.* This option uses the entered concentration data, plus the measured pH and alkalinity. This option is useful when reliable lab/field pH and alkalinity values are available. The alkalinity is the Total Alkalinity, representing all proton-accepting species down to 4.5 pH. The software adjusts the HCl and CO<sub>2</sub> amounts until the calculated pH and alkalinity match the measured values.
- 4. *Measured pH Only.* This option uses the entered concentration data and the measured pH. This option is useful when reliable lab/field pH values are available. The software adjusts the HCl amount until the calculated pH matches the measured value.
- 5. *Measured pH, Alkalinity and TIC.* This option uses the concentration data, plus the measured pH, alkalinity and Total Inorganic Carbon (TIC). This option is useful when there is a clear distinction between the organic and inorganic carbon contribution to alkalinity. The alkalinity is the Total Alkalinity, representing all proton-accepting species down to 4.5 pH. The software adjusts the HCI, Acetic Acid, and CO<sub>2</sub> amounts until the calculated pH, alkalinity and TIC match the measured values.

You will use the default Concentration Data Only option for this case.

✓ Select the Calculate button or press the <F9> key



We can also see a more detailed view of the calculation's progress, along with non-convergence messages, in the **Calculation Output** pane (if active) at the bottom of the screen.

The calculated pH and alkalinity differ slightly from the measured values. It is possible to adjust these using the **Measured pH and Alkalinity** option, but it is not part of this example. Three additional properties, density, conductivity, and TDS are shown in this grid.

concile Data Entry		Calculate Brine Properties Using: Oconcentration Data Only Gas-Phase CO2 Content (mole%) Measured pH and Alkalinity Measured pH Only Measured pH, Alkalinity, TIC Calculate Alkalinity	Specs	Calculate 🥥
e e		Properties	Measured	Calculated
Ľ 🕊	Г	Temperature (°C)	25.0000	
	Г	Pressure (atm)	1.00000	
	Г	pН	7.67000	7.52490
	Г	Alkalinity (mg HCO3/L)	0.0	581.942
	Г	Density (g/ml)	1.06400	1.06204
		Elec Cond, specific (µmho/cm)	0.0	1.25468e5
		Total Dissolved Solids (mg/L)	96280.0	N/A
		Compo	sition Adjustments	
		Add Charge Balance (mg/L Na+1)		115.954

Notice that the Total Dissolved Solids (TDS) were not calculated. This is because the by default the TDS calculation is turned OFF. If you want to see the calculated value, go to the Calculation Options icon for right click on the Olympus 1 Brine and select Calculation Options. Then rerun the case to see the calculated TDS value.

ScaleChem Tra	ining	scriptior
	Arrange	>
	Cut	
	Сору	
	Paste	
	Delete	
	Rename	
Actions Actions	Add As Stream	
🔛 Add Brine An	Clear Results	
🔶 Add Oil Anal	Clear Status	
≪P Add Gas Ana → Add Saturato	Calculation Options	

The complete set of results are in the Report tab.

✓ Select the Report tab



✓ Review the **Phase Properties** table

Phase Properties				
Parameter	Liquid-1			
pН	7.52048			
Density (g/ml)	1.06205			
Specific Electrical Conductivity (µmho/cm)	1.25468e5			
Ionic Strength (x-based) (mol/mol)	0.0289452			
Ionic Strength (m-based) (mol/kg)	1.70311			
Viscosity, absolute (cP)	1.05345			
Thermal Conductivity (cal/hr m °C)	513.589			
Alkalinity (mg HCO3/L)	581.942			
Hardness (mg/L of Mg+2 and Ca+2)	741.587			

The pH and alkalinity are reported here, along with additional properties of this 1-liter brine sample.

Pre and Post Scaling Tendencies					
Scale Mineral	Pre-scaling	Pre-index	Post-scaling	Post-index	
BaCO3 (Witherite)	0.0166206	-1.77935	0.0166206	-1.77935	
BaSO4 (Barite)	7.70045	0.886516	7.70045	0.886516	
CaCO3 (Calcite)	6.04691	0.781534	6.04691	0.781534	
CaSO4.2H2O (Gypsum)	0.0179836	-1.74512	0.0179836	-1.74512	
CaSO4 (Anhydrite)	0.0154017	-1.81243	0.0154017	-1.81243	
KCI (sylvite)	6.52714e-4	-3.18528	6.52714e-4	-3.18528	
NaCl (Halite)	0.0310960	-1.50730	0.0310960	-1.50730	
SiO2 (lechatelierite)	0.167156	-0.776877	0.167156	-0.776877	
SrCO3 (Strontianite)	2.55686	0.407706	2.55686	0.407706	
SrSO4 (Celestine (celestite))	0.118157	-0.927541	0.118157	-0.927541	

#### ✓ View the Pre and Post Scaling Tendencies table next

Olympus 1 Scaling Tendencies with Solids Off

The software computes that  $BaSO_4$ ,  $CaCO_3$ , and  $SrCO_3$  are supersaturated (S>1) in this sample (see Pre-scaling values). The remaining minerals are sub-saturated (S<1). No solids form because the Brine Analysis object has solids-formation turned off by default.

What are scaling tendencies?

- The Scale Mineral column lists species with pre-scale tendencies of at least 1×10<sup>-4</sup>.
- The **Pre-scaling** column is the thermodynamic driving force for precipitation. It represents the conditions at time=0, meaning conditions before any precipitation can commence. This value is based on the following relationship (shown for CaCO<sub>3</sub>):  $S_{CaCO_3} = \frac{a_{Ca} + 2a_{CO_3} - 2}{K_{SD_3} - 2}$ .

- The *Pre-Index* column is the base-10 logarithm of the pre-scaling tendency.
- The *Post-Scaling* and *Post-Index* columns are the scaling tendency values after the precipitation process is complete. It represents conditions at time=∞, when solids reach equilibrium with the water.

If we allowed solids to form, the table would also have a *Max scale* column showing solid concentration, per liter of brine, if the brine reached equilibrium.

#### ✓ Scroll down to the **Brine Composition** table.

Prine Composition

Cations	Value (mg/L)	Anions	Value (mg/L)	Neutrals	Value (mg/L)	
K(+1)	300.000	CI(-1)	57000.0	C02	11.5742	
Na(+1)	36116.0	HCO3- (*)	583.953	SiO2	15.0247	
Ba(+2)	5.00000	SO4-2	250.350			
Ca(+2)	600.000					
Mg(+2)	150.000					
Sr(+2)	80.0000					

Olympus 1 Brine Composition with Solids Off

This table contains the dissolved species concentration in the brine. It will be identical to what is added, because the brine is a single-phase. If solids were allowed to precipitate in the calculation, then the concentrations would have deviate from the initial values.

## Task 2 – Create a New Scale Scenario Calculation

The next task is to calculate the scaling potential during production. This is done using the *Scale Scenario* object. The software computes the tendencies and mass for each mineral at each location created. Results are presented in plots.

 Select Calculations > ScaleChem > Add Scenario from the menu, or double-click on the Add Scale Scenario icon in the Actions pane



The software adds a Scale Scenario object to the navigation panel and opens to the Design screen.



There are three vertical tabs: *Inlets, Conditions,* and *Solid*. You will work in each section to set up the calculation.

🎻 Des	scr	iption 🤮 Design 🛍 P	lot 髮 Report		
_	_				
ts		Туре	Na	me	Flow
nle	Г	<select></select>			
Inditions					
olid Co	D	etail Info of Selected Inlet Name			
ŭ	Π	Componer	nt	V	alue (mol/hr)

Initial Design screen of a newly added Scale Scenario object

✓ Rename the object *Olympus 1 Production* (select the Description tab or press the <F2>)

🛷 Des	scription	🥸 Design	🛍 Plot	5
Name:	Olympus 1 i	Production		

- ✓ Select the **Design** screen then the **Inlets** tab
- ✓ Click on the cell in the **Type** column to activate a dropdown list. Select **Brine** (m3/day)

The focus will automatically switch to the Name column.

✓ Select the Olympus 1 Brine from the dropdown menu in the Name column

✓ Enter 200 (m3/day) in the **Flow** column

ts		Туре	Name	Flow
nle	Г	Brine (m3/day)	Olympus 1 Brine	200.000
_		<select></select>		

• When an inlet row is active, the Detail Info of <u>the</u> grid at the bottom of the Inlets screen displays the composition of the inlet we selected. In our case, this is the *Olympus 1 Brine* composition.

ts	Туре	Nar	ne	Flow
nle	Brine (m3/day)	Olympus 1 Brine		200.000
_	<select></select>			
su				
ditio				
ŏ				
0				
핕	Reconciled Composition of Brine (C	lympus 1 Brine)		
й	Compone	nt	v	/alue (mg/L)
	H2O			9.66700e5
	BaO			5.58252
	CaO			839.524
	C02			432.762
	HCI			1342.44
	К20			361.382
	MgO			248.741
	NaCl			91810.7
	S03			208.363
	SrO			94.6080
		Phase Flow	Properties	
	Mass - Liquid-1 (Mass %)			99.9999
	Mass - Vapor (Mass %)			0.0
	Mass - Liquid-2 (Mass %)			0.0
	Moles (True) - Liquid-1 (Mole %)	)		100.000
	Moles (True) - Vapor (Mole %)			0.0
	Moles (True) - Liquid-2 (Mole %)	)		0.0
	Volume - Liquid-1 (Volume %)			100.000
	Volume - Vapor (Volume %)			0.0
	Volume - Liquid-2 (Volume %)			0.0

✓ Select the **Conditions** tab (vertical blue tab on the left side of the Design screen)

The Conditions tab contains 4 columns: Location, Temperature, Pressure, and Drop Solids.

✓ Type in the following conditions or use the dropdown menu within the Location cells

Location	Temp (° C)	Press (bar)
Reservoir	125	275
Bottom hole	125	260
Downhole	115	190
Midwell	105	130
Wellhead	100	100
Choke	90	80
Separator	60	30

The location cell contains a dropdown menu with commonly used locations, like reservoir, wellhead, separator etc. You can use one of these names or type in a name. A location name is required.

s		Location	Temperature (°C	Pressure (bar)	Drop Solids
let	Г	Reservoir	125.000	275.000	
<u> </u>		Bottom hole	125.000	260.000	
	Г	Downhole	115.000	190.000	
Suc	Г	Midwell	105.000	130.000	
ij	Г	Wellhead	100.000	100.000	
puo	Г	Choke	90.0000	80.0000	
ŭ	Г	Separator	60.0000	30.0000	
	Г	<enter location="" name=""></enter>			

A diagram appears below displaying the order of the locations that are entered. This screen has options for zooming, auto steps, sorting by temperature or pressure, and dropping solids.



- ✓ Select the vertical (red) Solid tab and
- ✓ Check the **Standard** box (to allow these solids to precipitate)

Inlets	Solids Selection Standard imu ■ BaSO4 (Barite)	Calculate 🖌
	CaCO3 (Calcite)	Summary
ditions	CaSO4 (Anhydrite) ·····☑ CaSO4.2H2O (Gypsum) ·····☑ NaCl (Halite)	Unit Set: Scale Metric
Con	SrSO4 (celestine (celestite)) 	Automatic Chemistry Model MSE-SRK (H3O+ ion) Databanks:
P		MSE-SRK (H3O+ ion) MSE (H3O+ ion)
Soli		Second Liquid phase Excluding 119 solid phases Using Helgeson Direct
		Inlets: Brine Olympus 1 (m3/day) Brine

✓ Press the Calculate button

#### ✓ Select the Plot tab



The default plot is the pre-Scale tendencies for the five dominant solids, including Calcite and Barite. Several minerals are computed to be supersaturated in the reservoir and at other production locations.

✓ Select the View Data button



The *View Data* button displays the results table. In some cases, this is an easier way to interpret the results.

	LOCATIONS	CaCO3 (Calcite)	CaCO3 (Aragonite)	SrCO3 (Strontianit e)	BaSO4 (Barite)	H2O
		Pre-ST	Pre-ST	Pre-ST	Pre-ST	Pre-ST
1	Reservoir	14.5214	11.7871	2.29611	0.805475	0.318622
2	Bottom hole	14.8382	12.0291	2.36814	0.817053	0.318777
3	Downhole	14.1441	11.3388	2.56862	0.972683	0.343902
4	Midwell	13.3416	10.5805	2.72714	1.16489	0.371855
5	Wellhead	12.9844	10.2397	2.81279	1.28329	0.387054
6	Choke	11.6034	9.07806	2.75562	1.51766	0.419389
7	Separator	8.41174	6.41208	2.61605	2.82421	0.540563

✓ Select the Variables button

😣 💽 🛛 View Data	Variables	Options
-----------------	-----------	---------

 Remove all the variables in the Y1 Axis field by clicking on the Y1 Axis title bar then pressing the double left arrows. Or, double-click on the variable you want to remove

	Y1 Axis
	Dominant Pre-scaling Tendencies
>>	
<	

✓ Open the Solid category and move CaCO3 and BaSO4 to the Y1 Axis by double-clicking the name

Select Data To Plot				?	×
Curves	^	>>	X Axis Locations		
Phase How Properties     Thermodynamic Properties     Pre-scaling Index     Scaling Index     Scaling Index     Scaling Index     Liquid-1     Vapor		>>	CaCO3 (Calcite) - Sol		
B- Liquid-2 B- Solid Dominant Solid BaSO4 (Bante) B- Molecular Totals	*	>>	Y2 Axis		

✓ Next, expand Additional Stream Parameters and move *pH* - Aqueous to the Y2 Axis by using the double arrow >> next to the Y2 axis

✓ Press **OK** and view the Data Table

	LOCATIONS	CaCO3 (Calcite)	BaSO4 (Barite)	pН
		mg/L	mg/L	
1	Reservoir	267.344	0.0	6.14491
2	Bottom hole	268.729	0.0	6.14576
3	Downhole	255.565	0.0	6.17858
4	Midwell	241.019	1.16756	6.21687
5	Wellhead	233.656	1.81190	6.23846
6	Choke	214.347	2.80491	6.28636
7	Separator	198.481	3.88369	6.34286

#### ✓ Select the View Plot button



According to the calculation, significant amounts of calcite precipitate in the reservoir and the amount decreases at each subsequent calculation as temperature and pressure decreases. The values shown in the plot are the <u>maximum</u> amounts of solids that will form at that location. No assumption is made that these solids <u>actually</u> form at each location (this requires a fluid dynamic and deposition model). Rather all scale mass moves with the fluid to the next calculation unless specified to deposit using the **Drop Solids** button in the **Conditions** tab.

The calculated pH increases during production. This is for two reasons. The first is that as less calcite precipitates, more alkaline  $CO_3^{-2}$  remains in solution. The second is that lower temperatures causes the pH of a solution to be higher.

✓ Save the file

## Summary

The instructions provided in this chapter are the most basic ScaleChem calculation. It is a two-step process, adding a brine and calculating its scaling potential as the well is produced. You will see in the following chapters that adding additional details to this basic scenario can increase reliability to the predictions.

## Chapter 3 – Olympus Gas Analysis

## Overview

This chapter introduces the *Gas Analysis* object. It is a very simple object with a limited number of functions. It is designed in a way that a user can enter conveniently, their gas analysis. You will continue working within the created file in *Chapter 2*.

## Task 3 – Create a New Gas Analysis

✓ Double-click on the Add Gas Analysis object in the Actions Panel

Add Gas Analysis

This adds a Gas object to the Navigator panel.

✓ Select the Description tab, then rename the object Olympus Gas



#### ✓ Select the Design tab

The names view of the Gas Analysis is defaulted to *Formula* view. Also, the Standard list of components extends to C6 alkanes. This is satisfactory for the gas analysis you will enter.

✓ Enter the following composition and values in the Inflows grid:

Olympus 1 Gas							
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 of the two below, depending on the Names view you select.

Component	Value	Normalized
	Subtotal: 10	Subtotal: 100.0
Water	1.80000	1.80000
Nitrogen	3.00000	3.00000
Carbon dioxide	1.50000	1.50000
Hydrogen sulfide	0.500000	0.500000
Methane	65.5000	65.5000
Ethane	14.0000	14.0000
Propane	8.00000	8.00000
Isobutane	1.00000	1.00000
n-Butane	3.00000	3.00000
Isopentane	0.500000	0.500000
n-Pentane	0.700000	0.700000
n-Hexane	0.500000	0.500000

Component	Value	Normalized
	Subtotal: 10	Subtotal: 100.0
H20	1.80000	1.80000
N2	3.00000	3.00000
C02	1.50000	1.50000
H2S	0.500000	0.500000
CH4	65.5000	65.5000
C2H6	14.0000	14.0000
СЗН8	8.00000	8.00000
i-C4H10	1.00000	1.00000
n-C4H10	3.00000	3.00000
i-C5H12	0.500000	0.500000
n-C5H12	0.700000	0.700000
C6H14	0.500000	0.500000

**Olympus 1 Gas Inflows in Display Name View** 

Olympus 1 Gas Inflows in Formula View

This is the extent of the gas entry step. There are modifications that can be part of this step, but in this scenario, they are not considered. Now that the gas is entered, the Olympus scale scenario will be recomputed.

## Task 4 – Recalculate the Scale Scenario with the Gas

The gas analysis was missing from the Scale Scenario calculation performed in Chapter 2. The net effect was that calcite was computed to be supersaturated. This is because the impact of gas-phase on the brine composition was not considered. You will see that by including the gas phase, the calcite scale risk will change considerably.

✓ Select the *Olympus 1 Production* icon in the Navigator pane



- ✓ Select the **Design** tab (horizontal tab) if not automatically sent there
- ✓ Select the Inlets tab (vertical) if not automatically sent there
- ✓ Click the **Type** cell in the 2<sup>nd</sup> row and select **Gas** from the drop-down list

ŝ	Туре	Name	Flow
let	Brine (m3/day)	Olympus 1 Brine	200.000
=	<select></select>		
$\mathbf{\mathbf{N}}$	Whole Fluid		
	Brine		
ű	Gas		
	2		

✓ The Name cell should display automatically the available gases. There should be one only, Olympus 1 Gas, select it.

• If the Olympus gas is not present in the drop-down cell, this is an indication that the Gas Analysis Object is using a thermodynamic model different from the Brine Analysis object. Make certain that the Gas Analysis and Brine Analysis objects are both using the MSESRK (H3O+ ion) framework. ✓ Enter a flow rate of 250 std E3m3/day in the Flow cell

<u>s</u>	Туре	Name	Flow
let	Brine (m3/day)	Olympus 1 Brine	200.000
=	Gas (std E3m3/day)	Olympus 1 Gas	250.000
	<select></select>		

- ✓ Calculate (Press the **<F9>** key)
- Select the Plot tab
   Plot

The plot will be displaying the last set of variables that you added, Calcite solids and pH. You will change this back to the default plot variables, the Dominant Scale Tendencies.

✓ Double-Click on the [Default Plot] item in the Plot Manager window. This is in the lower left of the screen



This will cause the plot to return to the default variables (and settings).



#### Pre-Scaling Tendencies Including Brine and Gas Analyses

The plot differs from the one computed at the end of Chapter 2 (see below). This is because the gasphase CO<sub>2</sub> introduces acid (carbonic acid) to the water. This causes the pH to decrease, which in turn reduces the  $CO_3^{-2}$  ion concentration. This result is that the scaling tendencies for the three carbonate solids (Calcite, Aragonite, and Strontanite) decrease.



Pre-Scaling Tendencies Including Only Brine Analysis

✓ Change over to View Data



The saturation of Calcite at reservoir conditions is now S $\approx$ 0.6, or twenty-three-times lower than the S $\approx$ 14.5 in Chapter 2.

	LOCATIONS	BaSO4 (Barite)	CaCO3 (Calcite)	CaCO3 (Aragonite)	H2O	SrSO4 (Celestine (celestite))
		Pre-ST	Pre-ST	Pre-ST	Pre-ST	Pre-ST
1	Reservoir	0.845065	0.632258	0.513209	0.317762	0.224134
2	Bottom hole	0.856086	0.660133	0.535160	0.317940	0.229413
3	Downhole	1.00600	0.645060	0.517122	0.343238	0.229675
4	Midwell	1.19131	0.649711	0.515252	0.371361	0.226253
5	Wellhead	1.30559	0.688080	0.542633	0.386648	0.224659
6	Choke	1.53388	0.610343	0.477510	0.419092	0.207854
7	Separator	2.81204	0.525997	0.400955	0.540600	0.162319

Notice that there is no longer any calcite scale, because it is now sub-saturated throughout the production line. The next step is to quantify the impact of the gas on the pH.

✓ Open the Variables window



- ✓ Double-click on the Y1 Axis variables to remove it
- ✓ Add pH to the Y1 axis (pH is in the Additional Stream Parameters category)

	~	
Calculation Parameters	>> Locations	
	,	
Additional Stream Parameters	Y1 Avie	
Density	oH	
Density Liq1	pri	
Density Solid	>N.	
Density Vap		
DIELEC Liq1	<<	
HARDNESS		
- IS Liq1		
- IS Lig1		
Std Lig Vol Lig1		
- Std Lig Vol Solid	Y2 Avie	
- Std Lig Vol Vap	12700	
VapFrac		
Phase Flow Properties	✓ >>	
_ + · · · · · · · · · · · · · · · · · ·	<<	
Standard V		
Use short names		
Hide zero species	Z Axis	
Plot data which is only within temperature range.	- Select -	

- ✓ Click **OK** to close the window
- ✓ Change to View Plot

Notice that the pH range of this calculation is about 0.5 units below that of Chapter 2. This again, is caused by including the  $CO_2$ -containing gas phase in the scale scenario.



 $\checkmark$ 

### Summary

A more representative scale scenario is achieved when the gas phase is included in the study. This is because brine production is in contact with the hydrocarbon phase, and by including it in the scale calculation, its impact on overall scale formation can be part of the scale risk analysis.

Calcite is also computed to be sub-saturated in the reservoir. This may, or may not be the case, depending on the reservoir mineralogy/cementation. In the next chapter we will investigate the impact of setting the gas and brine phase in equilibrium with the reservoir minerals, and its effect on mineral scaling.

## Chapter 4 – Olympus Reservoir Saturation

## **Overview**

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 CaCO<sub>3</sub>, CaSO<sub>4</sub>.H<sub>2</sub>O, FeCO<sub>3</sub>, and NaCl. This is based on the assumption that as the reservoir fluid flows through the rock pores, there is sufficient time to interact with the surface minerals and that this interaction occurs across the complete vertical production zone (the composition of the liquid flowing into the well does not vary with depth). The effect is that a single fluid composition flows into the well and this liquid+gas fluid is in equilibrium with the reservoir minerals.

This particular **Olympus** well produces from calcite-cemented sandstone. Barite is also present in minor quantities in the rock matrix. It is reasonable therefore, to saturate the fluid with calcite at reservoir conditions. This will cause  $Ca^{+2}$  and  $CO_3^{-2}$  to be added to the fluid and this revised brine composition will now be different from what was entered in Chapter 2. Because there is a composition change, you will create a new fluid called **Olympus 1 Reservoir**. This is a gas+brine fluid combination that will be used instead of the brine and gas analysis entered in the previous chapters.

To complete Chapter 4, you will need to have completed Chapters 2 and 3 first.

### Task 5 – Add a Saturator Calculation

 $\checkmark$  Open the Course file you used to compete Chapter 2 and 3.

This file should look like the following.



✓ Click on the Add Saturator icon from the Actions panel <sup>♣</sup> Add Saturator

The Saturator appears in the Navigator panel.

✓ Select the **Description** tag to rename the object **Olympus 1 Reservoir** 



#### ✓ Select the **Design** tab

• The Saturator has two vertical tabs, **Inlets** and **Solid**. Fluids are entered in the top grid and Conditions are entered in the bottom grid of the **Inlets** tab. Solids are selected and saturated in the **Solid** tab.

✓ Use the pull-down menus to select the following Fluid types, names, and flow rates

Olympus 1 Reservoir							
Type Name Flow							
Brine (m3day)	Olympus 1 Brine	200					
Gas (std E3m3/day) Olympus Gas 250							

✓ Enter the Reservoir conditions of 125°C and 275 bar in the **Conditions** section

ets	Г	Туре	Name	Flow
Ξ	Г	Brine (m3/day)	Olympus 1 Brine	200.000
		Gas (std E3m3/day)	Olympus 1 Gas	250.000
T		<select></select>		
3				
		C	Value	
		Temperature (°C)	125.000	
		Pressure (bar)		275.000

✓ Select the **Solid** (blue) tab

Saturating the fluid with minerals is a two-step process. The first step is selecting in the upper section of the window (**Solid Selection**), and then selecting it to saturate in the lower section of the window (**Reservoir Mineral Saturation Section**).

Solid	CaCO3 (Calcite) CaSO4 (Anhydrite CaSO4, 2H2O (Gy VaCl (Halite) SrSO4 (Celestine Expanded E-V All	:) psum) (celestite))
	Reservoir Mineral Saturation Section	
	Mineral to saturate	Inflow to vary

The upper section instructs the software to allow the selected solids to precipitate – to include the 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 column (**Mineral to saturate**) where the saturating mineral is selected. The second column (**Inflow to vary**) is the cation and anion to be adjusted. The image below has barite and calcite as saturating solids, and  $Ba^{+2}$ ,  $SO_4^{-2}$ ,  $Ca^{+2}$ , and  $CO_3^{-2}$  as being adjusted.

Mineral to saturate	Inflow to vary
BaSO4 (Barite)	BaSO4
CaCO3 (Calcite)	CaCO3
<select solid=""></select>	

For example, if barite is computed to be initially sub-saturated, then  $BaSO_4$ , in the form of  $Ba^{+2}$  and  $SO_4^{-2}$  ions are added in stoichiometric amounts until barite saturation is achieved. Stoichiometric amounts are required so the water maintains a charge balance.

By comparison, if Calcite is computed to be initially supersaturated, then stoichiometric amounts of  $Ca^{+2}$  and  $CO_3^{-2}$  are removed from the fluid until calcite is at saturation. Thus, the inflows will be positive if the solid is sub-saturated and negative if the solid is supersaturated.

✓ Select the **Standard** checkbox

ets	Solid Selection (check solids allowed to form)
르	Standard
	BaSO4 (Barite)
-	CaCO3 (Calcite)
.≝	CaSO4 (Anhydrite)
S	CaSO4.2H2O (Gypsum)
	NaCl (Halite)
	SrSO4 (Celestine (celestite))

At this point, you will notice that the Calculate button is yellow Calculate O. This is because no minerals have been selected to saturate the fluid. A warning also appears in the in the Summary

Warning: no solid selected for box Olympus 1 Reservoir. A yellow button is allowable, and a calculation may continue; it is merely a warning that the case is incomplete.

✓ In the **Reservoir Mineral Saturation Section** use the Solid drop-down menus to select BaSO4 (Barite) and CaCO3 (Calcite) as **Mineral to saturate** 



✓ Use the Inflow drop-down menu to select BaSO₄ and CaCO₃ as Inflow to vary (it should have been selected automatically).

Reservoir Mineral Saturation Section						
	Mineral to saturate	Inflow to vary				
Г	BaSO4 (Barite)	BaSO4				
	CaCO3 (Calcite)	CaCO3	$\sim$			
	<select solid=""></select>	CaCO3 Ba(HCO3)2 CaCl2 CaCO3 Ca(HSO4)2.2H2SO4 Ca(HSO4)2.2H2SO4 Ca(HCO3)2 Ca(HSO4)2 Ca(HSO4)2 CaCl2.2MgCl2	~			
		Ca(OH)2	$\mathbf{v}$			

The **Inflow to vary** list is lengthy because there are many ways of adding  $Ba^{+2}$ ,  $SO4^{-2}$ ,  $Ca^{+2}$ , and  $CO_3^{-2}$ . Deciding on which inflows to vary depends on the user's assessment of the fluid composition and which concentration is the most appropriate to change.

At this point, the Calculate button is green indicating that the specifications are complete.

- ✓ Calculate (or press the <F9> key)
- ✓ Click the **Report** tab Seport

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.

The key table is the **Saturation Details**. This contains the explicit Inflow changes. In this example, 102.4 mg/L CaCO<sub>3</sub> is added to the system (i.e. 41 mg/L Ca<sup>+2</sup> and 61.4 mg/L CO<sub>3</sub><sup>-2</sup>). Likewise, 1.5 mg/L BaSO<sub>4</sub> was added (i.e. 0.9 mg/L Ba<sup>+2</sup> and 0.6 mg/L SO<sub>4</sub><sup>-2</sup>).

Saturation Details:								
Solid	Inflow	Initial (mg/L)*	Final (mg/L)*	Delta (mg/L)				
BaSO4 (Barite)	BaSO4	8.07037	9.52380	1.45344				
CaCO3 (Calcite)	CaCO3	1423.06	1525.47	102.410				

#### ✓ Scroll down to the **Pre and Post Scaling Tendencies** table

Pre and Post Scaling Tendencies

Formula	Mineral	Excess Solute	Excess Solute	Pre-Scale	Pre-Scale	Post-Scale	Post-Scale
		mg/L	lb/1000bbl	S, ST	SI, Index	S, ST	SI, Index
SiO2	lechatelierite			0.0188198	-1.72539	0.0188198	-1.72539
BaCO3	Witherite			7.07139e-4	-3.15050	7.07137e-4	-3.15050
Mg(OH)2	Brucite			6.00466e-4	-3.22151	6.00467e-4	-3.22151
NaCl	Halite	0.0	0.0	0.0254531	-1.59426	0.0254530	-1.59426
BaSO4	Barite	2.65993e-5	9.32322e-6	1.00000	1.74560e-6	1.00000	0.0
SrSO4	Celestine (celestite)	0.0	0.0	0.223483	-0.650756	0.223483	-0.650756
SrCO3	Strontianite			0.139128	-0.856584	0.139128	-0.856584
CaCO3	Calcite	1.14067e-5	3.99812e-6	1.00000	1.09144e-7	1.00000	0.0
CaSO4.2H2O	Gypsum	0.0	0.0	0.0245117	-1.61063	0.0245117	-1.61063
CaSO4	Anhydrite	0.0	0.0	0.0985987	-1.00613	0.0985987	-1.00613
KCI	sylvite			1.31298e-4	-3.88174	1.31298e-4	-3.88174

The **Excess Solute** column shows that trace amounts of BaSO<sub>4</sub> and CaCO<sub>3</sub> 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 BaSO<sub>4</sub> and CaCO<sub>3</sub> inflows until it reaches these targets. These part-per-trillion values may look arbitrary, but in fact the values are equivalent to  $1 \times 10^{-10}$  moles of solid/kg water.

The pre-scale tendency for  $BaSO_4$  and  $CaCO_3$  equal 1.0 – by definition. That is, these are not calculated; they are defined. The remaining scale tendencies are computed.

#### ✓ Scroll down to the **Brine Composition** table

3rine Composition								
Cations	Value (mg/L)	Anions	Value (mg/L)	Neutrals	Value (mg/L)			
K(+1)	284.919	CI(-1)	54134.6	CO2	660.014			
Na(+1)	34300.4	HCO3- (*)	486.767	H2S	528.730			
Ba(+2)	5.60384	SO4-2	238.364	SiO2	14.2694			
Ca(+2)	610.845			N2	69.6510			
Mg(+2)	142.459			C1	1085.88			
Sr(+2)	75.9783			C2	202.244			
				C3	77.0591			
				nC4	17.5590			
				C6	0.389003			
				C5	1.18776			
				iC5	1.35485			
				iC4	6.29535			

The dissolved Cl<sup>-</sup> is computed to be ~54000 mg/L. This is lower than the ~57000 mg/L entered initially in the **Olympus 1 Brine** Analysis. There are two reasons for this. First, the water volume increased because of thermal expansion (125 °C vs. 25 °C); and second, because the dissolved gases have increased the liquid volume (this is a smaller effect).

This volume expansion can be seen in the **Phase Properties** table. The volume at reservoir conditions is ~210.6 m<sup>3</sup>. At standard conditions, this liquid occupies ~201.4 m<sup>3</sup>. The thermal expansion effect is the difference between 210.6 and 201.4 m<sup>3</sup>, and the dissolved gas effect is the difference between 210.4 m<sup>3</sup> added.

Phase Properties				
Parameter	Liquid-1	Vapor	Solid	
Volume Units	m3/day	E3m3/day	m3/day	
Volume	210.586	1.17971	2.13672e-9	
Volume, Std. Conditions Units	m3/day	std E3m3/day		
Volume, Std. Conditions	201.380	248.651		
Hardness (mg/L of Mg+2 and Ca+2)	744.033			

✓ Scroll down back to the Brine Composition table

Notice that the dissolved  $Ca^{+2}$  changed from 600 mg/L to ~611 mg/L. This is a combination of lower concentration due to liquid expansion, and an increased concentration because of the of the 41 mg/l  $Ca^{+2}$  added to saturate calcite.

Brine Composition					
Cations	Value (mg/L)	Anions	Value (mg/L)	Neutrals	Value (mg/L)
K(+1)	284.919	CI(-1)	54134.6	C02	660.014
Na(+1)	34300.4	HCO3- (*)	486.767	H2S	528.730
Ba(+2)	5.60384	SO4-2	238.364	SiO2	14.2694
Ca(+2)	610.845			N2	69.6510
Mg(+2)	142.459			C1	1085.88
Sr(+2)	75.9783			C2	202.244
				C3	77.0591
				nC4	17.5590
				C6	0.389003
				C5	1.18776
				iC5	1.35485
				iC4	6.29535

## Task 6 – Recalculate the Scale Scenario with the Saturated Reservoir

Considerable effort is taken to create a representative reservoir fluid. First, the *Brine* is entered, reconciled for charge balance, and if needed, reconciled for pH and alkalinity. Next, the gas composition is added, and the two fluids are set to equilibrium with each other and with important reservoir minerals. It is after these steps, and that a final scaling calculation is run.

The **Olympus 1 Reservoir** calculation contains the representative fluid. It is, therefore, this **Whole Fluid** (multiphase) that will be used in all subsequent calculations. You will see the **Whole Fluid** in the Type column of all ScaleChem calculations. When **Whole Fluid** is selected, all phases of this fluid are included.

You will use the Whole Fluid from the Reservoir to rerun the scaling calculations.

✓ Select the *Olympus 1 Production* in the Navigator Panel



- ✓ Select the **Design** tab and then the **Inlets** tab (if not already there)
- ✓ Select the gray cells to the left of the first two rows. This highlights the row. Then press the Delete key to remove the rows.

2	Туре	Name	Flow
let	Brine (m3/day)	Olympus 1 Brine	200.000
=	Gas (std E3m3/day)	Olympus 1 Gas	250.000
$\mathbf{i}$	<select></select>		

- ✓ With the inlets now empty, select Whole Fluid as the Type
- ✓ In the Name column, select *Olympus 1 Reservoir*

ŝ	Туре	Name	Flow
Inlet	Whole Fluid (m3/day)	Olympus 1 Reservoir	<automatic></automatic>
	<select></select>		

• The Flow cell should display <Automatic> , meaning that the fluid mass (and volume) computed in the reservoir is being transferred to this object.

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.

- ✓ The Conditions tab does not need to be edited since the Locations with their respective T and P had been previously entered
- ✓ Select the **Solid** tab and make sure the Standard box is checked



- ✓ Calculate (Or press <F9> key)
- ✓ Select the **Plot** tab and select **View Plot**
Click on the [Default Plot] entry in the Plot Template Manager to reset the plot to its default variables.



At Reservoir conditions (125°C and 275 atm), the Calcite and Barite pre-scaling tendency are 1.0 by design. As production moves up the tubing, pressure and temperature decrease. CaCO<sub>3</sub> scale tendencies decreases and reach a minimum at Separator conditions (60°C and 30 atm). Barite scaling tendencies increase at each location because the temperature decreases, and barite saturation is temperature sensitive.

✓ Save the file

# Summary

The *Saturator* is a tool for creating a representative reservoir fluid. This calculation constrains the fluid to be in equilibrium with the minerals selected. This causes the fluid composition to be fixed for those precipitating ions. It becomes a compositional starting point for computing scale risk.

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.

# Chapter 5 – Olympus Production Contour Plot

# **Overview**

An alternative to the *Scale Scenario* calculation is the *Contour Diagram*. The *Contour diagram* calculation studies a range of temperatures and pressures. By comparison, the *Scale Scenario* studies specific production locations (wellhead, GLV, PLT, etc.), and generally no more than ten are entered. The purpose for using this object is to then create a matrix of temperature and pressure conditions and overlay a fluid's properties, like scale tendencies, over it.

You will need to have completed Chapters 2 to 4 before starting this chapter.

## Task 7 – Create an Initial Contour Diagram

- ✓ Open the file used in Chapter 4.
- ✓ Add a Scale Contour by selecting Calculations > ScaleChem > Add Contour or doubleclicking on Add Scale Contour in the Actions Pane <sup>(®)</sup> Add Scale Contour
- ✓ Rename the object *Olympus 1 Contour*



- ✓ Select the Design tab
- ✓ Select Inlet grid and choose, and under the Type column, select Whole Fluid using the dropdown arrow

ţs	Туре	Name	Flow
nle	<select></select>		
_	Whole Fluid		
	Brine		
	Oil		
su	Gas		

- ✓ Select *Olympus 1 Reservoir* in the 2<sup>nd</sup> column
- ✓ Keep the <Automatic> flow rate option in the 3rd column

ţs		Туре	Name	Flow
lle	Г	Whole Fluid (m3/day)	Olympus 1 Reservoir	<automatic> 🗸</automatic>
ς- Ι		<select></select>		

#### ✓ Click the Conditions tab

You will set the minimum conditions to the Separator (60°C, 30 bar) and the maximum conditions to the Reservoir conditions (125°C, 275 bar). Also, to create a reasonable number of calculations (~900) and to keep the matrix somewhat symmetric, you will use increments of 2 °C and 10 bar.

#### **Temperature Range**

- ✓ Change the Start to 60 °C
- ✓ Change the End to 125 °C
- ✓ Select the Increment radio button Enter 2 as the increment

Temperatu	re kange		
		°C ~	
Start	60.0	Increment     2.0	]
End	125.0	O Number Steps 33	

#### **Pressure Range**

- ✓ Uncheck the Log box (if it is checked)
- ✓ Change the Start to 30 bar
- ✓ Change the End to 275 bar
- ✓ Select the Increment radio button (uncheck the Log box first)
- ✓ Change the Increment to 10

	oar 🗸 🗸
Start 30.0 Increme	nt 10.0
End 275.0 O Number	Steps 25

This action creates 33 temperature and 25 pressure steps and produces a calculation matrix of  $34 \times 26$  points, or 884 calculations. The calculation should take about fifteen minutes to converge, depending on the speed of your computer.

- ✓ Select the Solid tab
- ✓ Place a check next to the **Standard** box
- ✓ Save the file

Solids Selection				
Em Standard				
BaSO4 (Barite)				
CaCO3 (Calcite)				
CaSO4 (Anhydrite)				
CaSO4.2H2O (Gypsum)				
NaCl (Halite)				
SrSO4 (Celestine (celestite))				
Expanded				
i im ✓ All				

✓ Calculate



A Calculation Dialog appears displaying the calculation queue. Developers at OLI Systems, Inc. have accelerated this calculation by refining the solver algorithm and have reduced the amount of data stored, to limit the file size.



✓ When the calculation is complete, select the Plot tab

Diagram 1: Total Solid Concentration

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 (125°C and 275 bar). The lower left represents Separator conditions (60°C 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).

This plot is a pixilated map of the thermodynamic properties of a produced fluid. The property plotted by default is the **excess solids** (total solids concentration). Many other properties can be viewed, which will be explained in the next task.

## Task 8 – Exploring the Contour Variables

There are a number of fluid properties that are worth exploring. These properties help us to understand the fluid behavior as temperature and pressure change. The first two properties to review are the  $BaSO_4$  and  $CaCO_3$  pre-scaling tendencies followed by a common fluid property, pH.

✓ Select the Variables button on the top right of the diagram **•** View Data Variables Expand the Pre-scaling Tendencies category ✓ Double-click BaSO4 (Barite) Contour X Axis: Temperature Additional Stream Parameters Phase Flow Properties Pressure Y Axis: Thermodynamic Properties i liquid-1 🗄 Liquid-2 • Vapor Bolid Contour Variable Molecular Totals Scaling Tendencies BaSO4 (Barite) - Sol Pre-scaling tender >> Pre-scaling Tendencies CaCO3 (Calcite) - Sol Pre-scaling ter CaSO4 (Anhydrite) - Sol Pre-scaling CaSO4.2H2O (Gypsum) Pre-scaling NaCl (Halite) - Sol Pre-scaling tender ✓ Press the **OK** button and review the plot.



Diagram 2: BaSO<sub>4</sub> Pre-scaling Tendency

The contour colors change horizontally, indicating that barite scale tendency is temperature dependent, and increases as temperature decreases. The pressure dependence is much weaker, and it seem to indicate that scale tendency decreases as pressure decreases.

- ✓ Select the Variables button Select the Variables
- ✓ Expand the **Pre-scaling Tendencies** category then double-click CaCO3 (Calcite)



Diagram 3: CaCO<sub>3</sub> Pre-scaling Tendency

Calcite has both a temperature and pressure dependence. As temperature decreases, the scale tendency decreases, but as pressure decreases, the scale tendency increases. The latter is because  $CO_2$  degasses, which causes the pH to increase.

#### pH Diagram

- ✓ Select the Variables button View Data Variables
- ✓ Expand the Additional Stream Parameters category
- ✓ Double-click pH Aqueous



✓ Press OK



Diagram 4: pH -Aqueous

You will see an indistinguishable green plot. The scale to the right shows a range of 0 to 14 pH. This range is much greater than the pH range of the fluid, and needs to be modified in the **Plot Options**.

- ✓ Select **Options** button
- ✓ Click the **Contour** category
- ✓ Check the two Auto boxes for Minimum and Maximum

Customize Plot		?	×
Customize Plot Category General Legend X Axis Y Axis Contour	Scale       Auto     Value     Color (Hue)       Minimum     0.0     Image: Color (Hue)       Maximum     Image: Color (Hue)     Image: Color (Hue)       Schwarting     100     Image: Color (Hue)	?	×
	Saturation 100 Brightness 100 Logarithmic scale		
	OK Cancel Apply	Hel	P

✓ Press **OK** to close the window and view the plot



Diagram 5: pH – Aqueous

The pH is lower in the lower temperatures and higher pressures area in the top left of the diagram where the colors are the darkest red. At ambient temperatures, the pH jumps suddenly because of  $CO_2$  degassing at low pressures. We will evaluate the  $CO_2$  concentrations next.

• There is one point where the pH is computed to be 3.65. This is the result of a calculation error, that existed in V10.0. If you do not see this, then you are using a newer version.



✓ Press OK



Diagram 6: CO<sub>2</sub> – Liq1 Concentration

As expected, the dissolved CO<sub>2</sub> concentration changes with conditions. This is the key concentration that affects pH and calcite scale tendency.

#### CO2 (vap) K Value

You will next look at the equilibrium constant that governs  $CO_2$  solubility in the water. It is commonly referred to as the Henry's Constant (K<sub>H</sub>). At ideal activities, the following pressure relationship exists:

$$K_H P_{CO_2} = m_{CO_2}$$

This constant varies with temperature and pressure and this effect is visible in the Contour diagram.

- ✓ Select the Variables button
- ✓ Scroll down and expand the K-Values (m-based) category and select KCO2VAP: CO2VAP=CO2AQ

Activity Coefficients - Liquid-2 (m 🔺	X Axis: Temperature
Fugacity Coefficients - Vapor     Fugacities - Vapor	Y Axis: Pressure
Gibbs Free Energy	
Gibbs Free Energy Standard State	
Entropy	
Entropy Standard State (x-based)	Contour Variable:
K-Values - (x-based)	
H-Values - (m-based)	
• Mobilities	
Self Diffusivities - Liquid-1	
Self Diffusivities - Liquid-2	
Self Diffusivities - Vapor	
Molecular Apparent - Liquid-1	

✓ Press Ok, and review the plot



The diagram shows that  $K_H$  is highest at low temperatures and low pressures, and decreases moving from lower left to upper right. Thus, increasing pressure and temperature decreases the value of the constant, and thus decreases the intrinsic CO<sub>2</sub> solubility in water. CO<sub>2</sub> is therefore, least soluble at high pressure and high temperatures. This is one reason why CO<sub>2</sub> concentration in the water phases varies – there are others. For example, in *Diagram 6*, the region with the lowest CO<sub>2</sub> concentration is in the lower right, but the K<sub>CO2</sub> equilibrium, *Diagram 7*, has its lowest value in the upper right. Thus, there are additional factors controlling CO<sub>2</sub> solubility.

## Summary

This chapter introduced the *Contour Diagram* and discussed how one can use this in production applications. The contour diagrams are also used and to study the thermodynamic aspects of a given system.

# **Chapter 6 – Titan Production**

# **Overview**

Chapters 2 through 5 provided detailed instructions on using the following ScaleChem objects:

- Brine and Gas Analyses, Scale Scenario calculation (Chapters 2 to 3)
- Saturator Calculations (Chapter 4)
- Contour Scale Calculation (Chapter 5)

This chapter will cover the same calculation objects using fewer instructions. Its purpose is to reinforce what was learned in chapters 2 - 5 and to promote the anticipating of next-steps when using the interface. The chapter is divided into the following tasks:

Task 1 – Add a New Brine
Task 2 – Add a New Gas
Task 3 – Add a New Reservoir Saturator
Task 4 – Recalculate the Scale Scenario with Reservoir
Task 5 – Add a New Contour Diagram

The well is *Titan 1*, a hypothetical gas well with saline water (75000 mg/I TDS). The brine and gas compositions samples were taken after drilling the well. We will look at several aspects of this brine including, what scales may form during production, if solids will saturate at reservoir conditions, and how chemistry may change as pressure depletes.

**IT IS IMPORTANT**, that you do this work in the file you created for Chapter 2 to 5 (Olympus well). Doing so will eliminate complications in Chapter 7.

## Task 1 – Add a New Brine

- ✓ Open the SSC Basics file
- Add a new Brine Analysis 🗳 Add Brine Analysis
  - ---- 🐼 Olympus 1 Contour
- ✓ Label it Titan 1 Brine III Vitan 1 Brine

- ✓ Select the Design tab
- ✓ Enter the Brine Analysis (cations/anions/neutrals) from the table below in the Data Entry grid

Titan 1 Brine Analysis										
Cation	ns mg/l	Anions mg/l		Neutrals mg/l		Measured Data				
Na+1	30000	000 CI-1 45000 B(OH)3 100		100	Temperature (°C)	25				
K+1	600	SO4-2	50			Pressure (bar)	1			
Ca+2	+2 150 HCO3-1 420				рН	7.1				
Mg+2	9+2 150 C2H3O2-1 350			Alkalinity	550					
Sr+2	50									
Ba+2	Ba+2 25									
Fe+2	2									

✓ Select the **show non-zero** option and keep the default balance option as **Dominant Ion** 

	Π	Variable	Value	Balanced	Entry Options			
E.	Π	Cations (n	ng/L)		Units			
Data E		Na+1	30000.0	30000.0	mal			
					K+1	600.000	600.000	Display
		Ca+2	150.000	150.000	- I			
		Mg+2	150.000	150.000	Formula			
cile		Sr+2	50.0000	50.0000	Show Non-zero Only			
Co		Ba+2	25.0000	25.0000	Show Balanced Column			
Re	F	Fe+2	2.00000	2.00000	Touclete Mensory			
					remplate Manager			
		Anions (mg/L)			Standard $\checkmark$			
		CI-1	45000.0	47075.1				
		S04-2	50.0000	50.0000	Save as			
		HC03-1	420.000	420.000				
		C2H3O2-1	350.000	350.000	Balance Options			
					Туре			
		Neutrals (r	ng/L)		Dominant Ion			
		B(OH)3	100.000	100.000	Dominante zon			

- ✓ Select the Reconcile (blue) tab
- ✓ Enter the Measured Data from the table above (default temperature and pressure; 7.1 pH; 550 mg HCO3/L Alkalinity)
- ✓ Select the Measured pH and Alkalinity calculation option

oncile Data Entry		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			
e	Properties Temperature (°C)			Measured	Calculated	
<b>~</b>				25.0000		
		Pressure (atm)		1.00000		
		pH		7.10000		
		Alkalinity (mg HCO3/L)		550.000		
		Alkalinity End Point pH		4.50000		
	Density (g/ml)           Elec Cond, specific (µmho/cm)			0.0		
				0.0		
		Total Dissolved Solids (mg/L)		0.0		
		Compo	sitior	n Adjustments		
		Add Charge Balance (mg/L CI-1)				

The Alkalinity End Point pH will automatically display 4.5. This is the standard endpoint for a carbonate alkalinity experiment.

✓ Select the **Calculate** button or press the **<F9>** key

oncile Data Entry	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	- Si	ummary Unit Set: Metric (mass concentration) Automatic Chemistry Model MSE-SRK (H3O- ion) Databanks: MSE-SRK (H3O- ion) MSE (H3O+ ion) No Solid phase(s) Second Liquid phase Lision Helesson Direct	^			
Sec	Properties	Measured	Calculated		Stream Parameters:		
	Temperature (°C)	25.0000			Temperature (°C) 25 0000		
	Pressure (atm)	1.00000			Pressure (atm) 1 00000		
	pH	7.10000	7.10000	>	Stream amount (L) 1 00000		
	Alkalinity (mg HCO3/L)	550.000	550.000		Stream amount (E) 1.00000		
	Alkalinity End Point pH	4.50000			Dominant Ion Charge Balance (eg/L):		
	Density (g/ml)	0.0	1.05113		Cation Charge 1.34167		
	Elec Cond, specific (µmho/cm)	0.0	1.08160e5		Anion Charge -1.28314		
	Total Dissolved Solids (mg/L)	0.0	N/A		Imbalance 0.0585303		
	Compo	Composition Adjustments					
	Added titrant (mg/L) HCI		37.8553		CI-1 2075.075		
	Add carbonate (mg/L CO2)		-26.4185		Measured pH and Alkalinity.		
	Add Charge Balance (mg/L CI-1)		2075.08		Phase Amounts:		
					Liquid-1 (g) 1051.13	~	

 $\checkmark$  Save the file 📕

# Task 2 – Add a New Gas

✓ Add a new Gas Analysis <sup>⊕</sup> Add Gas Analysis

🗄 🖓 🙀 Titan 1 Brine

- ✓ Label it Titan 1 Gas → Titan 1 Gas
- ✓ Select the Expanded template

s.		Component	Value	Normalized	Entry Options	
8	Г		Subtotal: 0.	Subtotal: 100.	Units	
Ē		H2O	0.0	0.0	mole %	
		CH4	0.0	100.000	Display	
Reconcile		N2	0.0	0.0	Formula	
		F	CO2	0.0	0.0	
				H2S	0.0	0.0
		C2H6	0.0	0.0	Show Normalized Column	
		C3H8	0.0	0.0	Template Manager	
		i-C4H10	0.0	0.0		
		n-C4H10	0.0	0.0	Expanded 🗸 🗸	
		i-C5H12	0.0	0.0	Standard	
		n-C5H12	0.0	0.0	Expanded	
		C6H14	0.0	0.0		
		C7H16	0.0	0.0	Normalize Options	
		i-C8H18	0.0	0.0	Makeup 🗸	
		n-C8H18	0.0	0.0	Group Manager	
		C9H20	0.0	0.0		
		C10H22	0.0	0.0	Lose Groups Add	

✓ Enter the following gas composition

Formula	Component name	Mole %
H2O	Water	1.40
CH4	Methane	74.00
N2	Nitrogen	1.00
CO2	Carbon dioxide	1.50
C2H6	Ethane	6.40
C3H8	Propane	4.00
i-C4H10	Isobutane	3.00
n-C4H10	n-Butane	3.00
i-C5H12	Isopentane	2.00
C5H12	n-Pentane	2.00
C6H14	n-Hexane	0.50
C7H16	n-Heptane	0.40
iC8H18	Isooctane	0.30
C8H18	n-Octane	0.30
C9H20	n-Nonane	0.10
C10H22	n-Decane	0.10

## ✓ Check the Show Non-zero Only box

Component	Value	Normalized	Entry Options	Component	Value	Normalized	Entry Options
	Subtotal:	Subtotal: 10	Units		Subtotal:	Subtotal: 10	Units
Water	1.40000	1.40000	mole % 🗸 🗸	H2O	1.40000	1.40000	mole %
Methane	74.0000	74.0000	Display	CH4	74.0000	74.0000	Display
Nitrogen	1.00000	1.00000	Display Name	N2	1.00000	1.00000	Formula 🗸
Carbon dioxide	1.50000	1.50000	Display Nume .	CO2	1.50000	1.50000	r ormaid .
Ethane	6.40000	6.40000	Show Non-zero Only	C2H6	6.40000	6.40000	Show Non-zero Only
Propane	4.00000	4.00000	Show Normalized Column	C3H8	4.00000	4.00000	Show Normalized Column
Isobutane	3.00000	3.00000	Template Manager	i-C4H10	3.00000	3.00000	Template Manager
n-Butane	3.00000	3.00000	remplate rianager	n-C4H10	3.00000	3.00000	
Isopentane	2.00000	2.00000	Expanded $\checkmark$	i-C5H12	2.00000	2.00000	Expanded $\vee$
n-Pentane	2.00000	2.00000	Save as	n-C5H12	2.00000	2.00000	Save as
n-Hexane	0.500000	0.500000		C6H14	0.500000	0.500000	ourc com
n-Heptane	0.400000	0.400000		C7H16	0.400000	0.400000	
Isooctane	0.300000	0.300000	Normalize Options	i-C8H18	0.300000	0.300000	Normalize Options
n-Octane	0.300000	0.300000	Makeup $\checkmark$	n-C8H18	0.300000	0.300000	Makeup $\vee$
n-Nonane	0.100000	0.100000	Crown Manager	C9H20	0.100000	0.100000	Crown Manager
n-Decane	0.100000	0.100000	Ulse Groups Add	C10H22	0.100000	0.100000	Ulse Groups Add

Titan 1 Gas in Display Name View

Titan 1 Gas in Formula View

- ✓ Select the **Reconcile** (blue) tab
- ✓ Calculate
- ✓ Save the file

## Task 3 – Add a New Saturator

We do not necessarily know which species are likely to be saturated unless a mineralogy was provided. Therefore, using the saturator is a bit of an unknown factor. It is reasonable to create the saturator as before and select the standard solids but to not saturate a specific mineral. From this initial assessment, one can see which minerals are at or near saturation, and this can guide further decisions.

Add a Saturator The Add Saturator

🛓 🌍 Titan 1 Gas

- Label it Titan 1 Reservoir
   Titan 1 Reservoir
- $\checkmark$  Go to the **Design** tab and then to the **Inlets** (red) tab
- ✓ Add the *Titan 1 Brine* at a flow of 100 m3/day
- ✓ Add the *Titan 1 Gas* at 300 std E3m3/day

ets		Туре	Name	Flow
Ξ	Г	Brine (m3/day)	Titan 1 Brine	100.000
		Gas (std E3m3/day)	Titan 1 Gas	300.000

✓ Enter the Reservoir **Conditions** of 160°C and 470 bar

Conditions	Value
Temperature (°C)	160.000
Pressure (bar)	470.000

- ✓ Select the **Solid** (blue) tab
- ✓ Check the **Standard** solid box

ets	Solid Selection (check solids allowed to form)	
Ē	Standard	
-	CaCO3 (Calcite)	
Solic	CaSO4 (Anhydrite)	
	FeCO3 (Siderite)	
	NaCl (Halite)	
	Expanded	
	te⊻ Ali	

#### ✓ Calculate

## Review the pre-Scale Tendencies in the Report tab B Report

#### Pre and Post Scaling Tendencies

Formula	Mineral	Excess Solute	Excess Solute	Pre-Scale	Pre-Scale	Post-Scale	Post-Scale
		mg/L	lb/1000bbl	S, ST	SI, Index	S, ST	SI, Index
BaCO3	Witherite			2.66282e-3	-2.57466	2.66282e-3	-2.57466
Mg(OH)2	Brucite			6.82512e-3	-2.16589	6.82512e-3	-2.16589
NaCl	Halite	0.0	0.0	0.0175853	-1.75485	0.0175853	-1.75485
BaSO4	Barite	0.0	0.0	0.667204	-0.175742	0.667204	-0.175742
SrSO4	Celestine (celestite)	0.0	0.0	0.0380715	-1.41940	0.0380715	-1.41940
SrCO3	Strontianite			0.0751172	-1.12426	0.0751172	-1.12426
CaCO3	Calcite	0.0	0.0	0.324661	-0.488569	0.324661	-0.488569
CaSO4.2H2O	Gypsum	0.0	0.0	1.66865e-3	-2.77764	1.66865e-3	-2.77764
CaSO4	Anhydrite	0.0	0.0	0.0103396	-1.98550	0.0103396	-1.98550
KCI	sylvite			1.80909e-4	-3.74254	1.80909e-4	-3.74254
FeCO3	Siderite	0.0	0.0	0.0729053	-1.13724	0.0729053	-1.13724

Notice that  $BaSO_4$  is about 67% saturated,  $CaCO_3$  is about 32% saturated and  $FeCO_3$  is only about 7% saturated. Based on this results there is no need to saturate with solids, and we will keep our original water analysis.

So based on these results, would it be reasonable to saturate with all three solids? The only mineral that we could argue that we could saturate – to account for the worst case scenario – is Barite.

Solid Inlets	Solid Selection (check solids allowed to for Standard Sabor BasO4 (Barite) CaCO3 (Calcite) CaSO4 (Anhydrite CaSO4 (Anhydrite CaSO4 (Anhydrite) CaSO4 (Allow) FeCO3 (Siderite) NaCl (Halite) SrSO4 (Celestine ( SrSO4 (Celestine ( All	m) ) osum) (celestite))	Calculate Calculate Alkalinity Calculate Alkalinity Summary Unit Set: Scale Metric Automatic Chemistry Model MSE-SRK (H30+ ion) Databanks: MSE-SRK (H30+ ion) MSE (H30+ ion) Second Liquid phase Excluding 156 solid phases Using Helgeson Direct Inlets:
	Reservoir Mineral Saturation Section		Brine (m3/day) Brine 100.000
	Mineral to saturate	Inflow to vary	Gas (std Titan 1 E3m3/day) Gas
	<select solid=""></select>	D8504	Selected Solids:
			Solid To Saturate Inflow
			BaSO4 (Barite) Yes BaSO4

✓ Go back to the **Solids** tab, and select **Barite** as the mineral to saturate, and BaSO4 as the inflow to vary.

✓ Re-calculate

# ✓ Review the pre-Scale Tendencies in the Report tab <sup>™</sup> Report

Pre and Post Scalin	Pre and Post Scaling Tendencies								
Formula	Mineral	Excess Solute	Excess Solute	Pre-Scale	Pre-Scale	Post-Scale	Post-Scale		
		mg/L	lb/1000bbl	S, ST	SI, Index	S, ST	SI, Index		
BaCO3	Witherite			3.56563e-3	-2.44786	3.56562e-3	-2.44786		
Mg(OH)2	Brucite			6.82308e-3	-2.16602	6.82307e-3	-2.16602		
NaCl	Halite	0.0	0.0	0.0175844	-1.75487	0.0175844	-1.75487		
BaSO4	Barite	5.37051e-5	1.88240e-5	1.00000	2.03697e-7	1.00000	0.0		
SrSO4	Celestine (celestite)	0.0	0.0	0.0426291	-1.37029	0.0426291	-1.37029		
SrCO3	Strontianite			0.0751447	-1.12410	0.0751447	-1.12410		
CaCO3	Calcite	0.0	0.0	0.324528	-0.488748	0.324528	-0.488748		
CaSO4.2H2O	Gypsum	0.0	0.0	1.86695e-3	-2.72887	1.86695e-3	-2.72887		
CaSO4	Anhydrite	0.0	0.0	0.0115684	-1.93673	0.0115684	-1.93673		
KCI	sylvite			1.80897e-4	-3.74257	1.80897e-4	-3.74257		
FeCO3	Siderite	0.0	0.0	0.0729023	-1.13726	0.0729023	-1.13726		

Notice that now the fluid is saturated with Barite (Pre-Scale = 1.0).

Review the Brine Composition table. The original Ba+2 value has been overwritten to 32 mg/L.

✓ Save the file

## Task 4 – Add a New Scale Scenario

Once the reservoir fluid is prepared, the next step is to compute scaling up the production line.

- ✓ Add a Scale Scenario ∠ Add Scale Scenario
- 🔠 🛷 Titan 1 Reservoir
- ✓ Label it Titan 1 Scaling ↓ Titan 1 Production
- ✓ Enter Whole Fluid –*Titan 1 Reservoir* into the grid
- ✓ Keep the <Automatic> flow rate

ts	Туре	Name	Flow
nle	Whole Fluid (m3/day)	Titan 1 Reservoir	<automatic></automatic>
<u> </u>	<select></select>		

✓ Select the **Conditions** tab and enter the production conditions from the table below

s		Location	Temperature (°	Pressure (bar)	Drop Solids			
let	Г	Current Reservoir	160.000	470.000				
=		Perforations	160.000	450.000				
		2000 m	145.000	300.000				
ons		1000 m	130.000	220.000				
Ĕ		Wellhead	110.000	170.000				
Duc		Slug Catcher	110.000	140.000				
ŭ		Separator	70.0000	30.0000				
		<enter location="" name=""></enter>						

• Some of the names are not in the drop-down list. Therefore, type in the location names as necessary.

• If your data is in Excel, Word, or other tabular format then you can copy and paste it into the conditions grid. Conversely, this grid can be copied and pasted to another scale scenario, or to external program.

✓ Select the **Solid** tab then check the Standard box



- ✓ Select the Calculate button or press the <F9> key
- ✓ Select the Plot tab



The default plot shows pre-scaling tendencies for the five dominant scaling species.

The results indicate that **Barite** becomes supersaturated as the fluid moves through the different locations. Starts at ST=1.0, because we defined that the fluid is saturated at the reservoir – but as we are producing the fluid, the scaling risk increases up to 4 at the surface. This is indicating that as the fluid starts to cool down at the surface, we start seeing the supersaturation of Barite going up.

For a closer look at the solids that formed, we can adjust the plot parameters.



- ✓ Select the Y1 Axis header to highlight all the Y1 variables then select the << button to remove the current variable
- ✓ Expand the Solid category then double-click BaSO4 to add it to the Y1 Axis



✓ Press OK and view the Plot



Select the View Data button to see the solids' concentrations at each location
 View Data Variables

	Locations	BaSO4 (Barite) - Sol
		mg/L
1	Current Reservoir	0.0
2	Perforations	0.712545
3	2000 m	8.22231
4	1000 m	13.5677
5	Wellhead	19.7231
6	Slug Catcher	20.5841
7	Separator	35.5967

# Save the file

## Task 5 – Add a New Contour Diagram

You will create a Contour plot for the Titan 1 Reservoir to gain additional practice

- ✓ Add a Scale Contour <sup>®</sup> Add Scale Contour
  - 🗄 🛃 Titan 1 Production
- ✓ Add the Whole Fluid, *Titan 1 Reservoir*
- ✓ Keep the <Automatic> flow rate

ts		Туре	Name	Flow
nle	Γ	Whole Fluid (m3/day)	Titan 1 Reservoir	<automatic> 🗸</automatic>
_		<select></select>		

- ✓ Click the Conditions tab
- ✓ Change the settings as follows

Titan Contour				
Conditions	Start	End	Increment	Steps (calc)
Temperature, °C	70	160	2	45
Pressure, bar	40	470	10	43

Make sure to uncheck the Log box for the temperature and pressure range

✓ Select the **Solid** tab and select the Standard box



 $\checkmark$  Save the file before running  $\blacksquare$ 



✓ Calculate and look at the Plot



Titan Solid Concentration in Contour diagram

• There are four points where the total solid concentration is very high. These are the result of a calculation error, that existed in V10.0. If you do not see this, then you are using a newer version.

Notice that as pressure drops the scale concentration is computed to increase at higher temperatures. This plot is similar to the Olympus plot, and it can be inferred that the scale forming at lower pressures: a pressure-dependent scale, is either calcite, siderite, or both. The increased scale at lower temperatures (shade to darker blue moving to lower temperatures) is likewise, probably barite. That solid was shown to be temperature dependent in the Olympus case.

✓ We can confirm these inferences, by plotting the CaCO3, FeCO3, and BaSO4 variables in the Solids category.



# Summary

This chapter summarizes a production operation from start to finish. At this point, the calculation windows should start to look familiar and we should begin to anticipate the next steps.

# Chapter 7 – Titan-Olympus Mixing and Production Facilities

# **Overview**

This section presents a new calculation objects, *Facilities*. The Facilities is a simplified process simulator; it mixes and separates. It will be used to model the production facilities of the *Olympus* and *Titan* wells. Therefore, to this work, you must have completed Chapters 2 through 6 and have all calculations in the same file (you can download the file case from Chapter 2 through 6 <u>HERE</u>).

## Facilities Diagram

The diagram below is the production schematic for the Olympus and Titan fluids (gas, oil, brine). Both wells are produced to the same separation facility. The flow of each well was set in the previous chapters when you created the Saturator (Reservoir) object. These same flows are used in the facilities scenario. Each process unit in the schematic below are modeled as a *Node* in the facilities object. Nodes contain inlet and outlet streams and are isothermal calculations (fixed temperature and pressure). The nodes also have the capability to separate phases (gas, oil, and solid) from the brine stream. There are several nodes in the scenario below, and some of them are used as separators.



## Modeling the Surface Facilities of the Olympus and Titan Fields

In order to model this case realistically, we will start by adding a few additional waters to the file. Following that initial step, we will create the **Facilities** object

- Select Calculations > ScaleChem > Add Facilities or select the Add Facilities action icon \*\*: Add Facilities
- ✓ Label it Topside



✓ Select the **Design** tab

The top of the *Inflow Specs* screen shows node diagrams, which we build in the bottom half of the screen. For each node, we add conditions, inlets (i.e. brines or other nodes), and outlets (i.e. new nodes). We can also separate gas, oil, or drop solids.

Solid Conditions Inflow Specs	Node 1	•			Nodes are displayed here
	Node Input Name: Node 1 Add Delete	Drop Solids Zo	oom Reference	2	New nodes with their respective
	Con	ditions		Value	conditions are
	Pressure (bar)			15.0	added here
				1.01325	
	Туре	Name		Flow	Inflows are added
	<select></select>				here

1					_	
	#	Location	Temperature (°C)	Pressure (bar)	Туре	Name
	1	Titan Reservoir	160	470	Whole Fluid	Titan 1 Reservoir
	2	Titan Wellhead	110	170	Whole Fluid From	Titan Reservoir
	3	Titan Choke	110	140	Whole Fluid From	Titan Wellhead
	4	Olympus Reservoir	125	275	Whole Fluid	Olympus 1 Reservoir
	5	Olympus Wellhead	100	100	Whole Fluid From	Olympus Reservoir
	6	Olympus Choke	90	80	Whole Fluid From	Olympus Wellhead
	7	Manifold	100	100	Whole Fluid From	Olympus Choke
	'	Wannoid	100	100	Whole Fluid From	Titan Choke
	8	Flowline	80	90	Whole Fluid From	Manifold
	9	HP Separator	60	60	Whole Fluid From	Flowline
	10	LP Separator	50	20	Oil From	HP Separator
	11	Oil Heater	90	15	Oil From	LP Separator
					Gas From	HP Separator
	12	Gas Treatment	Gas Treatment 15	1	Gas From	LP Separator
					Gas From	Oil Heater
	13	Oil Treatment	15	1	Oil From	Oil Heater
					Brine From	HP Separator
					Brine From	LP Separator
	14	Water Treatment	15	1	Brine From	Oil Heater
					Brine From	Gas Treatment
					Brine From	Oil Treatment

The following table contains the conditions for each production location (nodes) in this example.

✓ Click on the Add button 14 times, to add 14 nodes for the corresponding locations



Next, we need to tell the software where the fluid is flowing through these nodes.

## Task 1 – Create the Titan Reservoir

✓ Double-click Node 1 then type *Titan Reservoir* as the name



After naming a node, we work in the Node Input area to enter its conditions and inflows.

- ✓ Enter Conditions of 160 °C and 470 bar
- ✓ Select Whole Fluid as the **Type** of fluid
- ✓ Select Titan 1 Reservoir in the Name column
- ✓ Keep the <Automatic> flow rate



We will continue to add more nodes.

• You also have the option to go to the **Conditions** tab to enter the names, T and P of each location.

✓ Go to the **Conditions** tab and enter the information given below

ecs	Γ	Node #	Name	Temperature (°C)	Pressure (bar)
S S	Г	1	Titan Reservoir	160.000	470.000
_§		2	Titan Wellhead	110.000	170.000
Ē		3	Titan Choke	110.000	140.000
		4	Olympus Reservoir	125.000	275.000
s		5	Olympus Wellhead	100.000	100.000
lei.		6 Olympus Choke		90.0000	80.0000
i je		7	Manifold	100.000	100.000
S I		8	Flowline	80.0000	90.0000
		9	HP Separator	60.0000	60.0000
		10	LP Separator	50.0000	20.0000
olid		11	Oil Heater	90.0000	15.0000
S		12	Gas Treatment	15.0000	1.00000
		13	Oil Treatment	15.0000	1.00000
		14	Water Treatment	15.0000	1.00000

✓ Go back to the Inflow Specs tab to complete the specifications for each node

## Task 2 – Titan Wellhead

- ✓ Select the *Titan Wellhead* node
- ✓ Confirm the Conditions of 110°C and 170 bar
- ✓ Select Whole Fluid from as the **Type** of fluid
- ✓ Select Titan Reservoir in the Name column
- ✓ The flow rate appears as Calculated



When an inflow to a node comes from another node, the Flow column is automatically calculated.

## Task 3 – Titan Choke

- ✓ Select *Titan Choke* node
- ✓ Confirm the Conditions of 110°C and 140 bar
- ✓ Select Whole Fluid from as the Type of fluid
- ✓ Select *Titan Wellhead* in the name column



## Task 4 – Olympus Reservoir

- ✓ Select the *Olympus Reservoir* node
- ✓ Confirm the **Conditions** of 125°C and 275 bar
- ✓ Select Whole Fluid as the Type of fluid
- ✓ Select Olympus 1 Reservoir in the Name column
- ✓ Keep the <Automatic> flow rate

Con	Value	
Temperature (°C)	125.0 275.0	
Pressure (bar)		
Туре	Name	Flow
Whole Fluid (m3/day)	Olympus 1 Reservoir	<automatic></automatic>

## Task 5 – Olympus Wellhead

- ✓ Select the *Olympus Wellhead* node
- ✓ Confirm the Conditions of 100°C and 100 bar
- ✓ Select Whole Fluid from as the **Type** of fluid

✓ Select *Olympus Reservoir* in the Name column

	Co	Conditions			
Γ	Temperature (°C)			100.0	
	Pressure (bar)			100.0	
	Туре	Name		Flow	
	Whole Fluid from (m3/day)	Olympus Reservoir		Calculated	

## Task 6 – Olympus Choke

- ✓ Select the Olympus Choke node
- ✓ Confirm the **Conditions** of 90°C and 80 bar
- ✓ Select Whole Fluid from as the **Type** of fluid
- ✓ Select Olympus Wellhead in the Name column

_			
í.	C	Value	
ſ	Temperature (°C)	90.	
	Pressure (bar)	80.0	
ſ	Туре	Name	Flow
	Whole Fluid from (m3/day)	Olympus Wellhead	Calculated
_			

## Task 7 – Manifold

- ✓ Select the *Manifold* node
- ✓ Enter conditions of 100°C and 100 bar
- ✓ We will enter now two inlets for this node:
  - In the first row, select Whole Fluid from as the Type of fluid, and then select Olympus Choke as the Name
  - In the second row, select Whole Fluid from as the Type of fluid, and then select Titan Choke as the Name

	Conditions			Value		
Г	Temperature (°C)			100.0		
	Pressure (bar)			100.0		
Γ	Туре	Name		Flow		
Г	Whole Fluid from (m3/day)	Titan Choke		Calculated		
Γ	Whole Fluid from (m3/day)	Olympus Choke		Calculated		

✓ The software will automatically calculate the flow for each brine

## Task 8 – Flowline

- ✓ Select the *Flowline* node
- ✓ Confirm the conditions of 80°C and 90 bar
- ✓ Select Whole Fluid from as the Type of fluid
- ✓ Select *Manifold* as the Name

Ē	Conditions			Value	
Г	Temperature (°C)			80.0	
	Pressure (bar)			90.0	
С	Туре	Name		Flow	
	Whole Fluid from (m3/day)	Manifold		Calculated	

## Task 9 – HP Separator

- ✓ Select the *HP Separator* node
- ✓ Confirm the **conditions** of 60°C and 60 bar
- ✓ Select Whole Fluid from as the **Type** of fluid
- ✓ Select *Flowline* as the Name

Γ	Conditions			Value	
Γ	Temperature (°C) Pressure (bar)			60.0	
				60.0	
Γ	Туре	Name		Flow	
	Whole Fluid from (m3/day)	Flowline		Calculated	

## Task 10 – LP Separator

- ✓ Select the *LP Separator* node
- ✓ Confirm the **conditions** of 50°C and 20 bar
- ✓ Select Oil from as the **Type** of fluid
- ✓ Select *HP Separator* as the Name

	Conditions			Value		
	Temperature (°C)			50.0		
	Pressure (bar)			20.0		
Ē	Туре	Name		Flow		
	Oil from (m3/day)	HP Separator	$\sim$	Calculated		

### Task 11 – Oil Heater

- ✓ Select the **Oil Heater** node
- ✓ Confirm the **conditions** of 90°C and 15 bar
- ✓ Select Oil from as the **Type** of fluid
- ✓ Select LP Separator as the Name

	Conditions			Value	
	Temperature (°C)			90.0	
	Pressure (bar)			15.0	
	Туре	Name		Flow	
	Oil from (m3/day)	LP Separator	$\sim$	Calculated	

## Task 12 – Gas Treatment

- ✓ Select the Gas Treatment node
- ✓ Confirm the conditions of 15°C and 1 bar
- ✓ We will enter three different gases for this node:
  - In the first row, select Gas from as the Type of fluid, and then select HP Separator as the Name
  - In the second row, select Gas from as the Type of fluid, and then select LP Separator as the Name
  - In the third row, select Gas from as the Type of fluid, and then select Oil Heater as the Name

] (	Value	
Temperature (°C)	15.0	
Pressure (bar)	1.0	
Туре	Flow	
Gas from (E3m3/day)	HP Separator	Calculated
Gas from (E3m3/day)	LP Separator	Calculated
Gas from (E3m3/day)	Oil Heater	Calculated

## Task 13 – Oil Treatment

- ✓ Select the Oil Treatment node
- ✓ Confirm the conditions of 15°C and 1 bar
- ✓ Select *Oil from* as the **Type** of fluid
- ✓ Select Oil Heater as the Name

	Con	Value	
	Temperature (°C)	15.0	
	Pressure (bar)		1.0
Ē	Туре	Name	 Flow
ſ	Oil from (m3/day)	Oil Heater	Calculated

## Task 14 – Water Disposal

- ✓ Select the Water Disposal node
- ✓ Confirm the **conditions** of 15<sup>o</sup>C and 1 bar
- ✓ We will enter three different brines for this node:
  - In the first row, select *Brine from* as the **Type** of fluid, and then select *HP Separator* as the **Name**
  - In the second row, select *Brine from* as the **Type** of fluid, and then select *LP Separator* as the **Name**
  - In the third row, select *Brine from* as the **Type** of fluid, and then select *Oil Heater* as the Name
  - In the fourth row, select *Brine from* as the **Type** of fluid, and then select *Gas Treatment* as the **Name**

In the fifth row, select *Brine from* as the **Type** of fluid, and then select *Oil Treatment* as the **Name**

	Con	Value	
Г	Temperature (°C)	15.0	
	Pressure (bar)	1.0	
	Туре	 Flow	
Г	Brine from (m3/day)	HP Separator	Calculated
	Brine from (m3/day)	LP Separator	Calculated
	Brine from (m3/day)	Oil Heater	Calculated
	Brine from (m3/day)	Gas Treatment	Calculated
	Brine from (m3/day)	Oil Treatment	Calculated

# Task 10 - Reviewing the process

After all the nodes are completed, the process should look like the image below.



**Note:** This application was meant to be basic mixing and separation with existing mass. There is no way to split stream, or recycles or controllers. That's in the domain of the process simulator.

- ✓ Save the file ■
- ✓ Select the Conditions (blue) tab

6				Temperat	Pressure	Drop	Calculate	Fluid	I Sent To N	ode#
ecc		Node #	Name	ure (°C)	(bar)	Solid	Alkalinity	Brine	Oil	Gas
ц С	Г	1	Titan Reservoir	160.000	470.000			2	2	2
<u>s</u>		2	Titan Wellhead	110.000	170.000			3	3	3
르		3	Titan Choke	110.000	140.000			7	7	7
		4	Olympus Reserv	125.000	275.000			5	5	5
s		5	Olympus Wellhea	100.000	100.000			6	6	6
Ei		6	Olympus Choke	90.0000	80.0000			7	7	7
ip		7	Manifold	100.000	100.000			8	8	8
Ū		8	Flowline	80.0000	90.0000			9	9	9
		9	HP Separator	60.0000	60.0000			14	10	12
		10	LP Separator	50.0000	20.0000			14	11	12
olid		11	Oil Heater	90.0000	15.0000			14	13	12
S		12	Gas Treatment	15.0000	1.00000			14		
		13	Oil Treatment	15.0000	1.00000			14		
		14	Water Treatment	15.0000	1.00000					

A summary of the process is shown in Conditions tab

- ✓ Select the **Solids** (red) tab
- ✓ Check the **Standard** box



- ✓ Click on the **Calculate** button
- ✓ Select the **Plot** tab when the calculation is complete



The default plot displays the standard **Pre-scaling Tendencies** vs locations. It is important to recognize that in this plot four different scenarios are shown. The results for Titan Reservoir, the results for the Olympus Reservoir, the results for mixing the fluids of these two reservoirs and separation, and the results for treatment.

For the Titan and Olympus reservoirs, we knew that they were going to be supersaturated with Barite at the surface. We see that when these two fluids are mixed together at the *Manifold* location, the scaling tendency start to increase. The Barite saturation at the HP Separator increases up to a value of 5.0. Additionally, notice that at the *Manifold* appears the risk of FeS scaling. The reason why we see the formation of this scale, is because the Olympus reservoir contained  $H_2S$  in the gas phase, while the Titan reservoir contained  $Fe^{+2}$  in the brine. As a result, we see supersaturation with FeS and the scaling risk increases as the fluid moves towards the *Separator*.

✓ Save the file ■

# Summary

This is a basic *Facilities* calculation. There are multiple uses for this function particularly when a full-fledged process simulator is too advanced for the application.

# Chapter 8 – Bathos P-101 Production

# **Overview**

Chapter 8 is a case modeled after a South Texas well. The **Bathos P-101** well produces a light oil (API 41) with an associated gas. The reservoir is a calcite-cemented sandstone at moderate temperature/pressure (93.3°C, 220.6 bar). The produced water contains about 50,000 mg/L TDS. The reservoir requires water injection, and a tertiary aquifer water with moderate incompatibility is currently the best choice. The injection and mixing scenario is also simulated.

## Setting up the OLI Studio File

- ✓ Start the OLI Studio and start working from a **new** file
- ✓ Before adding any objects, click on the top-level object in the Navigator Panel

Navigator	<del>Ļ</del>	٠	x	
SSC Basics - Chapter 08.oad				
🍫 Streams				

✓ Go to Calculations > Model Options



✓ Select the MSE-SRK (H3O+ ion) Thermodynamic Framework

Default Chemistry Model Options ?							
Databanks	Redox Phases T/P Span						
Databanks Thermodynamic Framework							

✓ Name the file **Bathos-GS Scenario** and Save the file

Navigator 👖 🔺 🗙	Rathon G	S Soonario
SSC Basics - Chapter 08.oad*	Daulos-G	is scenario
🍫 Bathos-GS Scenario	Description	Object Map
	Name: Bathos	-GS Scenario

## Task 1 – Create the Bathos P-101 Brine

The brine's composition is given in the table below.

Bathos P101 Brine Analysis								
Cations mg/L		Anio	ns mg/L	Neutrals	mg/L	Measured Propertie	es	
Na+1	15260	CI-1	24500	B(OH)3 107		Temperature	25⁰C	
K+	180	SO4-2	160	SiO2	60	Pressure	1 atm	
Ca+2	850	HCO3-1	See alkalinity*			рН	6.7	
Mg+2	135	C2H3O2-1	386			Alkalinity (mg (HCO3/L))	673	
Sr+2	65					Density (g/mL)	1.026	
Ba+2	1.3					Econd (µmho/cm)		
Fe+2	2.1					TDS (mg/l)		

\*This is case were the total alkalinity was measured, but not the inorganic carbon. A good initial/guess value for the bicarbonate ion then is the total alkalinity value.

- ✓ Add a Brine Analysis 🖳 Add Brine Analysis
- ✓ Label it Bathos P-101 Brine



- ✓ Select the **Design** tab
- ✓ Enter the composition from the table above in the Data Entry grid
- ✓ Select the Show Non-zero Only box
- ✓ Look in the lower right of the Summary box and note the charge balance output
|          | Variable        | Value     | Balanced | Entry Options                                       | - |
|----------|-----------------|-----------|----------|---|---|
| E        | Catio           | ns (mg/L) |          | Units Unit Set: Metric (mass concentration)         | 1 |
| a        | Na+1            | 15260.0   | 15260.0  | mal   | 1 |
| at       | K+1             | 180.000   | 180.000  | Automatic Chemistry Model                           |   |
| _ F      | Ca+2            | 850.000   | 850.000  | MSE-SRK (H30+ IOI) Databanks.<br>MSE-SRK (H30+ IOI) |   |
|          | Mg+2            | 135.000   | 135.000  | Formula V MSE (H3O+ ion)                            |   |
| -i e     | Sr+2            | 65.0000   | 65.0000  | Show Non-zero Only No Solid phase(s)                |   |
| <u>ğ</u> | Ba+2            | 1.30000   | 1.30000  | Show Balanced Column Using Helgeson Direct          |   |
| ě.       | Fe+2            | 2.10000   | 2.10000  | Stream Parameters:                                  |   |
|          |                 |           |          | Template Manager Temperature (°C) 25.0000           |   |
|          | Anions (mg/L)   |           |          | Standard V Pressure (atm) 1.00000                   |   |
|          | CI-1            | 24500.0   | 24908.5  | Stream amount (L) 1.00000                           |   |
|          | S04-2           | 160.000   | 160.000  | Save as Dominant Ion Charge Balance                 |   |
|          | HCO3-1          | 673.000   | 673.000  | (eq/L):   |   |
|          | C2H3O2-1        | 386.000   | 386.000  | Balance Options Cation Charge 0.723475              |   |
|          |                 |           |          | Type  |   |
|          | Neutrals (mg/L) |           |          | Imbalance 0.0115215                                 |   |
|          | SiO2            | 60.0000   | 60.0000  | Ion(s) needed to balance (mg/L):                    |   |
|          | B(OH)3          | 107.000   | 107.000  | > CI-1 408.471                                      |   |
|          |                 | $\sim$    |          | Measured pH and Alkalinity.                         |   |

The software added approximately 408.5 mg/L of Cl<sup>-</sup> to balance the charge imbalance of 0.012 eq/L. Notice in the Data Entry grid that the balanced Cl<sup>-</sup> concentration (yellow column) is 24908.5 mg/L.

- ✓ Select the **Reconcile** (blue) tab
- ✓ Enter the measured pH (6.7), Alkalinity (673), and density (1.026)
- ✓ Select the Measured pH and Alkalinity option

oncile Data Entry	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 🥥		
ec	Properties	Measured	Calculated	
<b>—</b>	Temperature (°C)	25.0000		
	Pressure (atm)	1.00000		
	pH	6.70000		
	Alkalinity (mg HCO3/L)	673.000		
	Alkalinity End Point pH	4.50000		
	Density (g/ml)	1.02600		
	Elec Cond, specific (µmho/cm)	0.0		
	Total Dissolved Solids (mg/L)	0.0		

**1** In this case we have a bicarbonate (HCO3-1) value that is different from the Alkalinity value. This is because the bicarbonate was measured separately from the organic acids. This means that we have enough information to distinguish between bicarbonate and alkalinity.

Properties	Measured	Calculated
Temperature (°C)	25.0000	
Pressure (atm)	1.00000	
pН	6.70000	6.70000
Alkalinity (mg HCO3/L)	673.000	673.000
Alkalinity End Point pH	4.50000	
Density (g/ml)	1.02600	1.02722
Elec Cond, specific (µmho/cm)	0.0	62973.9
Total Dissolved Solids (mg/L)	0.0	N/A
Compo	sition Adjustments	
Added titrant (mg/L) HCI		122.586
Add carbonate (mg/L CO2)		-66.9477
Add Charge Balance (mg/L CI-1)		408.471

✓ Click on the **Calculate** button or use the **<F9>** key

Notice that 408.5 mg/L of CI- were added to balance charge, 66.95 mg/L of inorganic carbon as  $CO_2$  were removed to balance alkalinity, and 122.6 mg/L of HCI were added to adjust pH.

# Task 2 – Create the Bathos P-101 Crude Oil

You will create an oil analysis using assay data.

- Add an Oil Analysis head Oil Analysis
- ✓ Label it Bathos P-101 Oil

The Oil Analysis's Design menu has four screens noted by a colored tab: **Combined** (orange) tab, **Pseudocomponents** (blue tab), **Assay** (red tab), and **Reconcile** (teal tab). Three of these tabs allow the user 3 different ways of entering data.

The **Combined** tab is used to enter pure components, the **Pseudocomponents** tab is used to enter the different pseudocomponents that make an oil sample, and the **Assay** tab that allows to enter a distillation curve.

✓ Click the **Assay** (red) tab

p	Component	Value	Normalized	^	Entry Options
ine	C13H28	0.0	0.0		Units
đ	C14H30	0.0	0.0		mole %
ပိ	C15H32	0.0	0.0		Display
	C16H34	0.0	0.0		Formula 🗸
	C17H36	0.0	0.0		
nts	C18H38	0.0	0.0		Show Non-zero Only
one l	C19H40	0.0	0.0		Show Normalized Column
Ē	C20H42	0.0	0.0		Template Manager
0	C21H44	0.0	0.0		
p	C22H46	0.0	0.0		Standard $\checkmark$
s	C23H48	0.0	0.0		Save as
	C24H50	0.0	0.0		
2	C25H52	0.0	0.0		
ŝaj	C30H62	0.0	0.0		Normalize Options
¥	C35H72	0.0	0.0		Prorate $\vee$
	C40H82	0.0	0.0		
e	нсоон	0.0	0.0		
nci l	C2H4O2	0.0	0.0		
5	C3H6O2	0.0	0.0		
٣	CH4O	0.0	0.0		
	C2H6O	0.0	0.0		
	CH2(OH)CH2(OH)	0.0	0.0		
	C4H8O2	0.0	0.0		
	(HCOOH)2	0.0	0.0		
	N2	0.0	0.0		
	C02	0.0	0.0		
	H2S	0.0	0.0		
				¥	

The Assay screen contains three data entry grids: Component, Entry Options and Distillation Data. The Appendix at the end of this chapter explains assay options in further detail.

	Component	Grid			
g	Component	mole %	Disti	llation D	ata Grid
nbine	<enter a="" name=""></enter>		Vo	lume%	Temperature (°F)
ocomponents Cor	Entry Options Type Entry Option Thermo Method Density 1.0 No. of Cuts	ons ~ ~ ~ 0			
Pseud	Display Assay Cu	ts			
ž	Assay Properties				
Asse	Name Mole % Mol	Wt. NBP (°F)	Sp Gr Cr	Tem Cr Pres	Cr Vol ( Acentric

The data to be entered is shown in the two tables below. The first table contain the assay specifications, name, fraction, measurement type, etc. The second table contains the experimental data.

Component						
Name	ASSAY					
Mole%	98.4					
Entry Options						
(experiment) Type	ASTM D86					
Thermo Method	API-8					
Density value	41					
Density units	API Gravity					
No. of Cuts	12					

Disti	<b>Distillation Data</b>				
Volume%	Temperature(°C)				
1	26				
5	41				
10	65				
20	88				
30	102				
40	129				
50	167				
60	208				
70	241				
80	279				
90	342				
95	358				
100	397				

Under **Component**, type the name ASSAY in the <Enter Assay Name> cell. Press the <Tab> key to move to the next cells.

The name cannot be longer than 5 characters.

Component	mole %
ASSAY	98.4000

✓ Enter the value, 98.4 in the **mole%** cell

This instructs the software that the assay represents 98.4% of the total hydrocarbon mass. The remaining 1.6% are inorganic gases CO2 and N2 – that we will enter in the **combined** tab.

# ✓ Change the Analysis Type to TBP CURVE

✓ Select API-8 as the Thermo Method

- ✓ Enter the value 41 in the **Density** box
- ✓ Select API Gravity
- ✓ Change the **No. of cuts** to 12
- ✓ Enter the Volume% and Temperature data from the given table above in the Distillation Data grid

Compon	ent	mole %	Assay is valid.		
ASSAY		98.4000	Volume%	Temperature (°C)	
1			1.00000	26.0000	
Entry Options			5.00000	41.0000	
Туре	TBP CUP	RVE 🗸	10.0000	65.0000	
Thermo Method	API-8	~	20.0000	88.0000	
	407.0		30.0000	102.000	
Density 41.00	API Gra	vity ~	40.0000	129.000	
No. of Cuts		12	50.0000	167.000	
			60.0000	208.000	
Display	Assay Cu	its	70.0000	241.000	
			80.0000	279.000	<b>.</b>

✓ Click on the **Display Assay Cuts** button

The Assay cuts are pseudocomponents. They combine to represent the overall crude oil. Each pseudocomponent has a name: "Assay\_NBPK", which is the name Assay you entered plus the normal boiling point in Kelvin. The next three columns are the molecular weight (**Mol Wt.**), boiling point (**NBP**), and specific gravity (**Sp Gr**) computed using the distillation data and the experimental type specification. The remaining columns are four key critical properties. There are a total of fourteen critical properties generated, and these are found in the individual tabs at the bottom of the table.

As	say Properties								
	Name	Mole %	Mol Wt.	NBP (°C)	Sp Gr	Cr Temp (°C)	Cr Pres (atm	Cr Vol (L/mol	Acentric Fact
Г	ASSAY_314K	11.9851	73.3433	40.5829	0.727398	223.052	40.9730	0.281535	0.205083
	ASSAY_347K	16.3730	87.6606	74.2516	0.752539	262.121	35.9749	0.333698	0.244386
	ASSAY_374K	20.6698	100.005	100.898	0.771307	292.288	32.8336	0.377727	0.276871
	ASSAY_406K	10.3190	116.217	133.071	0.792816	327.882	29.6739	0.434192	0.317963
	ASSAY_438K	7.89164	133.816	164.933	0.813025	362.248	27.0362	0.493745	0.356586
	ASSAY_470K	6.93183	152.965	196.560	0.832138	395.513	24.7809	0.556428	0.401241
	ASSAY_500K	7.50478	173.129	226.979	0.849727	426.748	22.8820	0.619958	0.446928
	ASSAY_531K	5.93787	195.643	258.005	0.866947	457.895	21.1696	0.687798	0.496418
	ASSAY_561K	3.64187	219.200	287.668	0.882794	487.067	19.7113	0.755235	0.546582
	ASSAY_593K	2.92961	247.338	319.950	0.899417	518.222	18.2936	0.831086	0.604470
	ASSAY_623K	3.86421	276.239	350.116	0.914415	546.854	17.1062	0.903883	0.661795
	ASSAY_655K	1.95133	309.376	381.595	0.929557	576.312	15.9887	0.981425	0.725084
s	ummary ASSAY	(_314K ASSAY	_347K ASSAY	_374K ASSAY	406K ASSAY	438K ASSAY	470K ASSAY	500K ASSAY	531K A + +

The next step is to add the inorganic data

✓ Click on the **Combined** tab

✓ Scroll down the list and look for N2 and CO2 and enter the following concentrations:

Component	Mole%
N2	0.5
CO2	1.1

#### ✓ Click on the **Show Non-zero** Only box

When done, the combined grid should look like the one below

<b>D</b>		Component	Value	Normalized	Entry Options
ine	Г	Inflows	Subtotal: 1.60000/	Subtotal: 1.60000/100.000 (mol	Units
đ		H2O	0.0	0.0	mole % 🗸
ပိ		N2	0.500000	0.500000	Display
	Г	CO2	1.10000	1.10000	Formula
	Г				
uts		Assay	Subtotal: 98.4000/	Subtotal: 98.4000/100.000 (mol	Show Non-zero Only
- Be		ASSAY	98.4000	98.4000	Show Normalized Column

## Task 3 – Add a Gas

- Add a Gas Analysis <sup>So</sup> Add Gas Analysis
- ✓ Label it Bathos P-101 Gas
- ✓ Make it 100 mole% CH4
- ✓ Click on the **Show Non-zero** Only box

( e		Component	Value	Normalized	Entry Options
<u>s</u>			Subtotal: 0.	Subtotal: 100.	Units
۲Ľ		H2O	0.0	0.0	mole % 🗸 🗸
		CH4	0.0	100.000	Display
e.	L				Formula $\checkmark$
Reconc					Show Non-zero Only Show Normalized Column

## Task 4 – Add a Saturator

You will combine the brine and oil analysis at reservoir conditions, and saturate the combined fluid with CaCO<sub>3</sub>.

Bathos P-101 Saturate			
Туре	Name	Flow	
Brine (bbl/day)	Bathos P101-Brine	850	
Oil (std bbl/day)	Bathos P-101-Oil	2200	
Gas (std Mft3/day)	Bathos P-101-Gas	300	
Reservoir Conditions			
Temperature, °F	200		
Pressure, barg	220		

✓ Add a Saturator – 基 Add Saturator

- ✓ Label it Bathos P-101 Reservoir
- ✓ Change the Reservoir Units to Scale English (select the Saturator object and then click on the units manager icon <sup>€</sup>;

Units Manager - Bathos P-101 Reservoir	?	×
Units Manager		
Scale English V Flowing V Conc.	~	·
Customize		
OK Cancel Apply	I	Help

✓ Click on the Customize button to change the units of pressure to **barg** 

t Units - Bathos P-101 Reservoir			?	×
	O Batch S	ystem	Flowing	System
mposition Parameters Corrosion Inlets				
Variable			Units	^
Temperature		°F		
Pressure		barg		$\sim$
Time		day		_
Alkaliaity		ma HCO	2/	_
		Ing HCO	SVL	_
Electrical Conductivity, molar		m2/ohm	mol	_
Specific Electrical Conductivity		umbo/cn	n	
Energy		Btu/dav		_
Energy, Molar		Btu/mol		_
Entropy		Btu/R da	iy	
Entropy, Molar		Btu/mol	R	
Fugacity		barg		
Heat Capacity		Btu/lb R		
lonic Strength (x-based)		mol/mol		
Ionic Strength (m hased)		mol/ka		

- ✓ Select the **Design** tab and then go to the **Inlets** tab
- ✓ Under **Type** enter Brine, Oil and Gas with the flows given in the above table

	_			
ete		Туре	Name	Flow
Ξ	Г	Brine (bbl/day)	Bathos P-101 Brine	850.000
	Г	Oil (std bbl/day)	Bathos P-101 Oil	2200.00
-	Г	Gas (std Mft3/day)	Bathos P-101 Gas	300.000
ile i		<select></select>		

✓ Enter the Bathos P-101 Reservoir conditions of 200°F and 3200 psia

	Conditions	Value
Г	Temperature (°F)	200.000
	Pressure (barg)	220.000

✓ Select the **Solid** tab a check in the **Standard** solids box



- ✓ Check the Calculate Alkalinity box
- ✓ Click on the Calculate or press the <F9> key

Calc <u>u</u> late 🥝
Calculate Alkalinity

• The calculate button will be yellow. This is indicating that solids need to be selected for saturation. However, for this case you will calculate the CaCO<sub>3</sub> scale tendency before saturating, to see how close it is to saturation. So, the Reservoir Mineral Saturation step will be skipped.

- ✓ Click on the **Report** tab and review the **Scale Tendencies** table.
- $\checkmark$  Let's analyze how far or close to saturation some of these minerals are.

#### Pre and Post Scaling Tendencies

Formula	Mineral	Excess Solute	Excess Solute	Pre-Scale
		mg/L	lb/1000bbl	S, ST
SiO2	lechatelierite			0.0739809
BaCO3	Witherite			1.56764e-4
FeCO3	Siderite	0.0	0.0	0.125334
NaCl	Halite	0.0	0.0	4.58379e-3
BaSO4	Barite	0.0	0.0	0.399215
SrSO4	Celestine (celestite)	0.0	0.0	0.135852
SrCO3	Strontianite			0.0877755
CaCO3	Calcite	0.0	0.0	0.753399
CaSO4.2H2O	Gypsum	0.0	0.0	0.0301403
CaSO4	Anhydrite	0.0	0.0	0.0695226

Calcite is about 75% of saturation. All other minerals are sub-saturated. So, it is reasonable to set this mineral to saturation to account for maximum risk conditions.

You were instructed to calculate alkalinity. This is because if calcite will be reservoir-saturated then the composition effects on properties should be monitored.

#### ✓ Record the calculated Alkalinity in the **Phase Properties** table.

Parameter	Liquid-1	Liquid-2
рН	5.72513	0.0
Mass (lb/day)	3.05878e5	6.46399e5
Moles (True) (Ibmol/day)	16689.6	5606.82
Density (lb/ft3)	62.5264	47.8116
Specific Electrical Conductivity (µmho/cm)	1.57078e5	0.0
lonic Strength (x-based) (mol/mol)	0.0133994	0.0
lonic Strength (m-based) (mol/kg)	0.763787	0.0
Viscosity, absolute (cP)	0.335132	2.86677
Thermal Conductivity (Btu/hr ft °F)	0.394353	0.0757889
Alkalinity (mg HCO3/L)	689.107	

## ✓ Return to the **Design** tab > **Solid** tab, and saturate Calcite by adding CaCO3 inflow

R	Reservoir Mineral Saturation Section				
		Mineral to saturate	Inflow to vary		
		CaCO3 (Calcite)	CaCO3	2	
		<select solid=""></select>			

✓ Calculate and review the top table in the report (Saturation Details)

Saturation Details:

Solid	Inflow	Initial (mg/L)*	Final (mg/L)*	Delta (mg/L)
CaCO3 (Calcite)	CaCO3	2070.86	2130.85	59.9824

According to the calculation, 60 mg/L CaCO<sub>3</sub> is added to saturate calcite mineral. This converts to 24 mg/L Ca<sup>+2</sup> and 36 mg/L CO<sub>3</sub><sup>-2</sup>.

The overall change is nominal to total dissolved Ca<sup>+2</sup>. It increases about 3%, from 850 mg/L to 874 mg/L.  $CO_3^{-2}$ , on the other hand, increases by 36 mg/L, which increases the alkalinity by ~13%, from 689 to 762 mg/l as  $HCO_3^{-1}$ .

Phase Properties			
Parameter	Liquid-1		
рН	5.78154		
Mass (lb/day)	3.05903e5		
Moles (True) (Ibmol/day)	16690.0		
Density (Ib/ft3)	62.5329		
Specific Electrical Conductivity (µmho/cm)	1.57132e5		
Ionic Strength (x-based) (mol/mol)	0.0134308		
Ionic Strength (m-based) (mol/kg)	0.765601		
Viscosity, absolute (cP)	0.335271		
Thermal Conductivity (Btu/hr ft °F)	0.394360		
Alkalinity (mg HCO3/L)	762.095		

The Ca<sup>+2</sup> change is small, and perhaps within the sampling, experimental, and fluid representation uncertainty. A Similar argument for the total alkalinity is less tenable.

So, this means that this was probably reasonable to saturate with Calcite.

The next analysis is to review the hydrocarbon tables, to review the data provided, including the water and  $CO_2$  content in the oil phase

#### ✓ Scroll down to the **Oil Composition** table

Components	Oil (mole %)	Components	Oil (mole %)
C4H8O4	6.64776e-10	ASSAY_314K	10.0939
C2H4O2	2.03442e-4	ASSAY_347K	13.7897
B(OH)3	1.21837e-4	ASSAY_374K	17.4088
C02	0.866836	ASSAY_406K	8.69098
H2O	0.492749	ASSAY_438K	6.64662
H2SO4	2.31657e-22	ASSAY_470K	5.83824
H4SiO4	8.30543e-8	ASSAY_500K	6.32080
HBO2	6.38007e-8	ASSAY_531K	5.00109
HCI	1.33788e-10	ASSAY_561K	3.06732
SiO2	2.24408e-3	ASSAY_593K	2.46742
SO3	2.53898e-31	ASSAY_623K	3.25457
CH4	13.9935	ASSAY_655K	1.64348
N2	0.421534		

The water content is 0.49 mole%. This water mass was transferred from the brine phase. The dissolved  $CO_2$  is 0.87%, which is less that the original value entered of 1.1% (in the oil composition). This reductions is due to the transfer of  $CO_2$  to the brine phase.

Lastly, check the brine volume (at standard conditions vs reservoir conditions) in the Phase Properties table.

Phase Properties						
Parameter	Liquid-1	Solid	Liquid-2			
pН	5.78154		0.0			
Mass (lb/day)	3.05903e5	5.29571e-6	6.46392e5			
Moles (True) (Ibmol/day)	16690.0	5.29109e-8	5606.68			
Density (Ib/ft3)	62.5329	169.192	47.8115			
Specific Electrical Conductivity (µmho/cm)	1.57132e5		0.0			
Ionic Strength (x-based) (mol/mol)	0.0134308		0.0			
Ionic Strength (m-based) (mol/kg)	0.765601		0.0			
Viscosity, absolute (cP)	0.335271		2.86693			
Thermal Conductivity (Btu/hr ft °F)	0.394360		0.0757888			
Alkalinity (mg HCO3/L)	762.095					
Volume Units	bbl/dayReservoir Conditions	ft3/day	bbl/day			
Volume	871.283	3.12999e-8	2407.95			
Volume, Std. Conditions Units	bbl/dayStandard Conditions		std bbl/day			
Volume, Std. Conditions	849.777		2323.50			
Hardness (mg/L of Mg+2 and Ca+2)	963.045					

Compare the values to the initial 850 bbl/day of Brine (added to the Saturator object). Notice that the difference between the flow measured at the separator vs the calculated at reservoir conditions is 21.28 bbl/day. This indicates that some water gets transferred to other phases along the production line.

Also notice that the results don't include the gas phase. This is because the gas phase has been condensed into the oil phase.

## Task 5 – Add a Scale Scenario

The final task is to calculate scaling tendencies.

- ✓ Add a Scale Scenario ∠ Add Scale Scenario
- ✓ Label it Bathos P-101 Scale Scenario
- Change the Scale Scenario Units to Scale English (select the Saturator object and then click on the units manager icon

Units Manager - Bathos P-101 Reservoir	?	×
Units Manager		
Scale English V Flowing V Conc.	~	F
Customize		
OK Cancel Apply	ł	Help

✓ Click on the Customize button to change the units of pressure to **barg** 

Variable	Units
Temperature	۴
Pressure	barg
Time	day
Alkalinity	ma HCO3/L
Density	lb/ft3
Electrical Conductivity, molar	m2/ohm-mol
Specific Electrical Conductivity	µmho/cm
Energy	Btu/day
Energy, Molar	Btu/mol
Entropy	Btu/R day
Entropy, Molar	Btu/mol R
Fugacity	barg
Heat Capacity	Btu/lb R
lonic Strength (x-based)	mol/mol
Ionic Strength (m based)	mol/ka

- ✓ Select the **Design** tab and then go to the **Inlets** tab
- ✓ Under Type select Whole Fluid, Bathos P-101 Reservoir, and <Automatic>

The grid should look like the one below.

<u>s</u>	Туре	Name	Flow
let	Whole Fluid (bbl/day)	Bathos P-101 Reservoir	<automatic> 🗸</automatic>
=	<select></select>		
	*		

✓ Select the **Conditions** tab, and enter the following information:

Location	Temp (°F)	Press (barg)	
<b>Original Reservoir</b>	200	220	
<b>Current Reservoir</b>	200	160	
Flowing Reservoir	200	150	
Bottomhole	200	147	
2600'	190	166	
1300'	180	80	
Wellhead	170	54	
Flowline	150	33	
Separator	140	9.3	

The screen should look like the one below:



✓ Select the Solid tab and select the Standard checkbox



- ✓ Calculate or press the <F9> key
- ✓ Select the Plot tab
- ✓ Open the Variables window and check all the boxes at the bottom of the window



Plot data which is only within temperature range.

✓ Close the window and review the results



Notice that overall there is not scale risk. There is saturation in the original, current and flowing reservoirs and in the Bottomhole.

Once you reach the 2600 location – the risk of calcite scale formation goes down. When you get to the flowline, nothing is supersaturated. But then you get to the Separator, Calcite gets slightly supersaturated.

Let's have a look at the amount of **solids.** 





You can see that the Original Reservoir has no scale risk. Overtime as the reservoir pressure drops, up to 27 mg/L of CaCO3 precipitates out of the fluid (current reservoir). As the fluid flows through the well (flowing reservoir) another 4 mg/L of CaCO3 precipitates out. The total material in the reservoir, i.e. the 32 mg/L of CaCO3, is assumed to stay in the rock itself. At the bottomhole, is where we will start seeing 33 mg/L of CaCO3 scale. At the other locations, everything else is computed to be sub-saturated, until we reach the Saturator, where 21 mg/L of CaCO3 precipitates out.

✓ Go to the **Report** tab, and look for the **Separator** results.

#### Location Name: Separator

Stream Properties					
Stream Amount	8641.60	bbl/day			
Temperature	140.000	°F			
Pressure	9.30000	barg			
Mass - Total	9.52295e5	lb/day			

Phase Properties

Parameter	Liquid-1	Vapor	Solid	Liquid-2
pН	6.13905			0.0
Mass (lb/day)	3.05704e5	14925.4	6.31776	6.31659e5
Moles (True) (Ibmol/day)	16683.1	728.028	0.0631225	4885.63
Density (lb/ft3)	63.2274	0.485325	169.192	48.8513
Specific Electrical Conductivity (µmho/cm)	1.09906e5			0.0
Ionic Strength (x-based) (mol/mol)	0.0134294			0.0
Ionic Strength (m-based) (mol/kg)	0.765014			0.0
Viscosity, absolute (cP)	0.511942	0.0125855		2.09297
Thermal Conductivity (Btu/hr ft °F)	0.374038	0.0214179		0.0648259
Volume Units	bbl/day	Mft3/day	ft3/day	bbl/day
Volume	861.153	30.7535	0.0373407	2302.99
Volume, Std. Conditions Units	bbl/day	std Mft3/day		std bbl/day
Volume, Std. Conditions	849.060	274.816		2214.00
Hardness (mg/L of Mg+2 and Ca+2)	970.687			

At the separator, the software computes that there are 4 phases present: water, vapor, solid and organic phase.

Since the fluids were measured at the separator, we want to make sure that the software is predicting the same measured values.

For the brine or liquid, we have that the software is predicting 849 bbl/day – and at the separator it was measured as 850 bbl/day. This is a good prediction.

For the organic phase, the software is predicting 2214 std bbl/day vs 2200 std bbl/day being produced.

And, for the gas phase, we had 300 std Mft/day being produced, vs 275 std Mft/day. So, we are off by about 8% here.

## ✓ Save the file

## Summary

This is another typical well, with similar procedures to previous chapters. The difference is that this chapter introduced the oil analysis object. There are a few errors that were overlooked, including the missing water in the oil analysis and the missing dissolved  $CO_2$  in the water. This could have been resolved by adjusting the two analyses, or by creating a makeup water or  $CO_2$  stream. Both options will be considered in the advanced section of the ScaleChem training manual.

### Appendix: Assay Entry Options

There are four Assay types. These are experimental methods used to create distillation curves.

Entry Op	otions		
Туре		ASTM D86	
5		ASTM D86	
Thermo Method		ASTM D1160	
Density	34.00	ASTM D2887 TBP CURVE	

- ASTM D86 runs at atmospheric pressures and is used for all oil types.
- ASTM D1160 runs at vacuum pressures and is used for heavy oils.
- ASTM D2887 runs on a gas chromatograph and is used for light oils.
- TBP CURVE refers to true boiling point curve.

There are four methods for calculating thermodynamic properties, API, Cavett and Lee-Kessler.



- 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.



- Specific Gravity is the ratio of the material density to water. Studio ScaleChem requires specific gravity to be between 0.228 and 1.6
- API Gravity is defined by the following equation:

$$API(60F) = \left(\frac{141.5}{SG(60F)}\right) - 131.5$$

• Watson K is a method that relates density to boiling point.

$$K = \frac{(NBP)^{\frac{2}{3}}}{SG}$$

# Chapter 9 – Injection Water Mixing in Bathos Reservoir

# Overview

A common question in production chemistry is whether injection water and reservoir fluid are compatible. In this chapter, we will look at how the OLI Studio: ScaleChem feature called *Mixing Water* can help answer this question. We will continue working with the **Bathos** case.

The *Mixing Water* feature calculates fluid properties when two brines are mixed. For this calculation, we select up to two brines to mix. We can also add a single *gas* or a single *oil* phase, and select solids. Then we designate whether the mix should take place by a flow rate or a ratio. The software changes the relative volumes of each fluid to create a combined fluid at the selected ratio or flow rate. The total brine, gas, or oil flow rates do not change during the calculation. The resulting plotting screen is identical to the scale scenario. We define the mixing ratio as the ratio of brine that comes from the first brine.

## Task 1 – Create an Injection Water

For this example, the injection water will be Seawater.

- ✓ Go to the menu and select View > Toolbars > Object Library
- ✓ From the Standard Objects window (that appear on the right-hand side of the window) select the option Sea Water



- ✓ Click on it and drag it to the Navigator Panel, and name it **Seawater**
- ✓ Change the *Thermodynamic Framework* of the Seawater to MSE-SRK

	_				
≥	Ц	Variable	Value	Balanced	Entry Options
Ĕ		Cations (m	Units		
aE		Na+1	10561.0	10564.0	ma A 🗸 🗸
Dat		K+1	380.000	380.000	Display
		Ca+2	400.000	400.000	
		Mg+2	1272.00	1272.00	Formula
cile		Sr+2	13.0000	13.0000	Show Non-zero Only
Col		Ba+2	0.0500000	0.0500000	Show Balanced Column
Re		Li+1	0.100000	0.100000	T
					i emplate Manager
		Anions (m	g/L)		Standard 🗸 🗸
		CI-1	18980.0	18980.0	Causas
		S04-2	2648.30	2648.30	Save as
		Br-1	65.0000	65.0000	
		B(OH)4-1	33.5500	33.5500	Balance Options
		F-1	1.40000	1.40000	Туре
		I-1	0.0500000	0.0500000	Dominant Ion
		HCO3-1	144.000	144.000	
		Neutrals (n	ng/L)		
		Si02	5.00000	5.00000	

- ✓ Select the **Reconcile** tab
- ✓ Select the **Concentration Data Only**
- ✓ Calculate then save the file

oncile Data Entry	Calculate Bri Concer Gas-Ph Measur Measur Measur Calcula	ne Properties Using: htration Data Only ase CO2 Content (mole%) ed pH and Alkalinity ed pH Only ed pH, Alkalinity, TIC te Alkalinity	Specs	solids to form	Calc <u>u</u> late 🥥
Sec		Properties		Measured	Calculated
	Temperature	(°C)		25.0000	
	Pressure (atr	Pressure (atm)		1.00000	
	pH			0.0	8.34511
	Alkalinity (mg	HCO3/L)		0.0	167.059
	Density (g/ml	)		0.0	1.02213
	Elec Cond, specific (µmho/cm)			0.0	50964.4
	Total Dissolved Solids (mg/L)		0.0	N/A	
			Com	position Adjustments	
	Add Charge	Balance (mg/L Na+1)			2.98982

The software added 2.99 mg/l Na+1 to balance the charge.

## Task 2 – Add a Mixing Water Calculation

We are going to assume seawater breakthrough and we are mixing at the. And in this case, we are mixing with the Bathos water.

- ✓ Add a Mixing Water calculation ¥<sup>Add Mixing Water</sup> and name it Seawater Injection Bathos
- ✓ Change the units of the Mixing water object to Scale English Units

Re 🛨 🔤 🖞 🔤 📩 🗤 🗄 🗰 🛨 🛟 🔊 🕋	N	
Units Manager - Seawater Injection - Bathos	?	×
Units Manager		
Scale English V Flowing V Conc.	~	·
Customize		
OK Cancel Apply	ł	Help

- ✓ In the Inlets tab, enter the First Brine, Seawater Injection Bathos
- ✓ For the Second Brine, select Bathos-P101 Reservoir

ſ	Туре	Name	Flow
I	First Brine (bbl/day)	Sea Water	2000.00
ĺ	Second Brine (bbl/day)	Bathos P-101 Reservoir 🗸 🗸	

• The *Mixing Water's Design* tab opens to the *Inlets* screen. It contains *First Brine*, *Second Brine*, and the standard *inflow* row. It is not entirely clear, but the flow cell on the First brine row is in fact the total flow of water = first + second brine (they are not separate).

The flow of the First Brine will be varied to do the mixing study, and it will appear in the x-axis in the default plots.

✓ Enter the mxing conditions of 200°F and 147 barg

ĺ	Conditions	Value
I	Temperature (°F)	200.000
I	Pressure (barg)	147.000

• The 147 barg is the injection well pressure, and this added pressure will impact the thermodynamic stability of the interfaces; oil-water and mineral-water.

- ✓ Select the Conditions tab
- ✓ Change the mix type to Ratio
- ✓ Change the Steps to **10**
- ✓ Press the Auto Step button

lets	Select Type			
-	Ratio 🗸			
s	Total flow: 2000.00 bbl/day			
Condition	Steps: 10 Auto Step			

When complete, the grid should look like the following. The first row represents 100% Seawater and the last row represents 100% Bathos brine at 10% intervals.

Brine Ratios	
Sea Water	Bathos P-101 Reservoir
1.00000	0.0
0.900000	0.100000
0.800000	0.200000
0.700000	0.300000
0.600000	0.400000
0.500000	0.500000
0.400000	0.600000
0.300000	0.700000
0.200000	0.800000
0.100000	0.900000
0.0	1.00000

✓ Select the **Solid** tab then check the **Standard** box



✓ Press <F9> to calculate and save the file

The plot should look like the one below



The plot shows that we could possibly form a Magnesium silicate phase (Mg3SiO2O5(OH)4. This is because now we are introducing other species that come with the seawater composition. However, this phase is not being formed (the amount of solids for this phase is zero), so we can remove it from the plot to make it easier to read.

Let's modify the plot to show the pre-scaling tendencies of interest.

- ✓ Click on the Variables button
- Remove the Dominant Pre-scaling Tendencies from the Y1 Axis and add the phases shown below, then click OK.



The plot should look like the image below.



So now, what we see here is the different results from no sea water (0%) to 100% sea water – which is the last point to the right.

Notice that if we inject 100% seawater into this reservoir **calcite** will be automatically supersaturated. You can also see that **barite** has a bell shape like curve, which is an indication of incompatibility. **Celestine** also shows a little hump at higher ratios and is another example of incompatibility. The other solids like **anhydrite** and **gypsum** have pre-scaling values below 1.0, so we don't have to worry about incompatibility. Therefore, mixing these two fluids at injection water will have incompatibility problems.

We can also study the amount of solids that are computed when we mix these two brines.

- ✓ Go to the Variables button
- ✓ Go to the **solids** category and select **barite**, **calcite** and **celestine**. Click OK.

The plot should look like the image below.



**Calcite** forms at both extremes – at 100% seawater and 100% bathos reservoir brine - **celestine** stats forming at about 30% sea water until 100% bathos fluid. **Barite** forms at almost all the ratios, with a small mineral concentration.

✓ Save the file

# Summary

The Mixing block is a basic tool for testing incompatible waters. It adjusts the flow of two brines and holds the remaining inflows (like oil or gas) constant. This is done at a single T/P condition and the total brine flow is fixed. More complicated mixing calculations are presented in later chapters.

# Chapter 10 – Offshore High-Pressure Gas Production with Low Water Cut

## **Overview**

This chapter is intended to reinforce the training elements of Chapters 2 through 6 and to introduce mass balance to production chemistry analyses. This case is of several offshore wells producing a gas-condensate. They produce a high gas-water ratio (GWR) fluid, and the production chemist is certain that the produced water sample collected has been diluted with condensed water from the gas phase. The water sample was taken at the separator, and the water production rate is based on flow from this unit.



The table below contains the production conditions that will be used in this case.

Variable	Value	Units
Water flow	28	m3/day @ separator
Gas flow	Gas flow 2100 Std E3m3/day at separ	
Separator Temperature	40	°C
Separator Pressure	60	bar
Reservoir Temperature	205	°C
Reservoir Pressure	1380	bar

To simplify the procedure, the wells are combined into one, and a single produced fluid is created. To make this simplification, the assumption is that the water and gas compositions and reservoir conditions are identical in each well.

## Task 1 – Add a Brine Analysis

- ✓ Launch the software or select File > New (if the software is already started) and Save as Chapter 10 – High GWR
- ✓ Click on Streams and change the name to High GWR production



✓ Select High GWR production and go to Chemistry > Model Options...

📧 File Edit Streams Calcula	tions	Chemistry	Tools	View	Wi	ndov
🗅 😅 🖬   X 🖻 💼   🍜	१ №	Pre-bu	uilt Mod	els	>	SIE.
Navigator 🛛 🗛 🔺 🗙		Templ	ates		>	F
SSC Basics - Chapter 10.oad*	De	Mode	l Option	s		
	N	ame: High G	WR prod	uction		

✓ Under the Databanks tab select the MSE-SRK (H3O+ ion) as the Thermodynamic Framework, and click OK.

Databanks	Redox	Phases	T/P Span		
Databan	ks				
	Thermodynamic Framework				
	MS	SE-SRK (H	H3O+ion)	~	•

- ✓ Add a Brine Analysis 🔛 Add Brine Analysis
- ✓ Label it Separator Water



✓ Enter the data from table below into the **Design** > **Data Entry** grid

Analysis of the water sampled at the separator								
Cations	tions Conc, mg/L Anions Conc, mg/L Neutrals Conc, mg/L		<b>Measured Properties</b>	Value				
Na+1	3600	CI-1	6350	B(OH)3	40	Temperature (°F)	100	
K+	27	SO4-2	1.5	(Boric acid)	18	Pressure (atm)	1	
Ca+2	550	HCO3-1	39.5			рН	6.9	
Mg+2	5					Alkalinity (mg HCO3/L)	44.5	
Sr+2	0.2					Density (g/mL)	1.1125	
Fe+2	1.6					Conductivity	n/a	
Ba+2	1.6					Total Dissolved Solids	174956	

The brine composition is simple. The pH and alkalinity are reported.

- ✓ Change the Entry Options to Formula to make components easier to enter
- ✓ After entering the data, check the Show Non-zero Only box Show Non-zero Only

Variable Value Balanced Entry Options Cations (mg/L) Units Na+1 3600.00 3600.00 mg/L  $\sim$ 27.0000 K+1 27.0000 Display 550.000 550.000 Ca+2 Formula  $\sim$ Mg+2 5.00000 5.00000 Sr+2 0.200000 0.200000 Show Non-zero Only Fe+2 1.60000 1.60000 Show Balanced Column 1.60000 Ba+2 1.60000 Template Manager Anions (mg/L) Standard  $\sim$ CI-1 6350.00 6542.68 Save as... SO4-2 1.50000 1.50000 39.5000 HCO3-1 39.5000 Balance Options Neutrals (mg/L) Type B(OH)3 18.0000 18.0000 Dominant Ion  $\sim$ 

The screen should look like the one below

- ✓ Click the **Reconcile** tab
- ✓ Add the Measured Properties from the table above (6.9 pH, Alkalinity of 44.5 mg HCO3/L, Density of 1.1125 g/mL, and TDS of 174956 mg/L)
- ✓ Select the Measured pH Only button and select the Calculate Alkalinity box
- ✓ Calculate

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	Calc <u>u</u> late 🥥
Properties	Measured	Calculated
Temperature (°F)	100.000	
Pressure (atm)	1.00000	
рН	6.90000	6.90000
Alkalinity (mg HCO3/L)	44.5000	35.6986
Density (g/ml)	1.11250	1.00081
Elec Cond, specific (µmho/cm)	0.0	23671.4
Total Dissolved Solids (mg/L)	1.74956e5	N/A
Compo	sition Adjustments	
Added titrant (mg/L) HCI		3.19309
Add Charge Balance (mg/L CI-1)		192.677

The computed pH now match the measured value. The density, alkalinity and conductivity are also computed.

## Task 2 – Add a Gas Analysis

The production gas is in the table below. It is a combination of light gas with some condensate components. We will enter the data into the Gas Analysis object.

Component	<b>Display Name</b>	Mole%
H2O	Water	0.0
N2	Nitrogen	1.0
CO2	Carbon dioxide	1.4
CH4	Methane	93.75
C2H6	Ethane	2.0
C3H8	Propane	0.8
i-C4H10	Isobutane	0.1
n-C4H10	n-Butane	0.2
i-C5H12	Isopentane	0.5
n-C5H12	n-Pentane	0.1
C6H14	n-Hexane	0.15

• There are several isomers and depending on your version, the *Formula* view may be indistinguishable. Change the display option to *Display Name* or *OLI Tag* if you encounter this problem.

- ✓ Add a Gas Analysis <sup>⊗</sup> Add Gas Analysis
- ✓ Label it Produced Gas

Navigator 🛛 🖡 🔺 🗙	Duradurand (	3	
SSC Basics - Chapter 10.oad*	SP Produced (	535	
🏘 High GWR production	🦪 Description	🛛 🥸 Design	🥸 Definiti
🗄 🖓 🙀 Separator Water			
🗄 🌍 Produced Gas	Name: Produced	Gas	

- ✓ Select the **Design** tab > **Inflows** tab
- ✓ Enter the data from Table 2 into the Inflow grid

Toggle the Display between **Display name** and **OLI Tag** if you need to distinguish between isomers

Display				
Formula	~			
Display Name				
Formula				
OLI Tag				

✓ Check the **show non-zero Only** option

The completed screen should look like the one below

Component	Value	Normalized	Entry Options
	Subtotal: 1	Subtotal: 100.	Units
H2O	0.0	0.0	mole %
N2	1.00000	1.00000	Display
CO2	1.40000	1.40000	Formula
CH4	93.7500	93.7500	
C2H6	2.00000	2.00000	Show Non-zero Only
C3H8	0.800000	0.800000	Show Normalized Column
i-C4H10	0.100000	0.100000	Template Manager
n-C4H10	0.200000	0.200000	·
i-C5H12	0.500000	0.500000	Standard $\checkmark$
n-C5H12	0.100000	0.100000	Save as
C6H14	0.150000	0.150000	

The gas-phase water content rarely given, but in this case it is important, because the gas-to water ratio is high. There are several ways to calculate the water content, which we will investigate in later chapters. For now, we will calculate the water content manually, by equilibrating it with the brine.

## Task 3a – Calculate the H<sub>2</sub>O Content in the Gas

We are given the fluid composition and conditions at the separator unit. We can start with the assumption that the hydrocarbon and brine are in equilibrium at this point. If this is true, then we can calculate the  $H_2O$  saturation concentration in the gas phase.

- ✓ Add a Saturator object 基 Add Saturator
- ✓ Label it Separator
- ✓ Add the following inlets, and flows

Туре	Name	Flow	Units
Brine	Separator Water	28	m3/day
Gas	Produced Gas	2100	Std E3m3/day

Your screen should look like the following

	_			
ets		Туре	Name	Flow
Ξ	Г	Brine (m3/day)	Separator Water	28.0000
	Г	Gas (std E3m3/day)	Produced Gas	2100.00

✓ Enter the Separator **Conditions**: 40°C and 60 bar

	Conditions	Value
Г	Temperature (°C)	40.0000
	Pressure (bar)	60.0000

✓ Calculate and when done Click the Report tab

✓ View the Volume in the **Phase Properties** table (results may differ)

Phase Properties			
Parameter	Liquid-1	Vapor	
рН	4.73902		
Mass (kg/day)	25608.2	1.57242e6	
Moles (True) (kgmol/day)	1414.27	89201.3	
Density (g/ml)	1.00257	0.0451143	
Specific Electrical Conductivity (µmho/cm)	26720.3		
Ionic Strength (x-based) (mol/mol)	3.94420e-3		
Ionic Strength (m-based) (mol/kg)	0.220757		
Viscosity, absolute (cP)	0.670076	0.0129268	
Thermal Conductivity (cal/hr m °C)	542.579	32.8228	
Volume Units	m3/day	E3m3/day	
Volume	25.5424	34.8542	
Volume, Std. Conditions Units	m3/day	std E3m3/day	
Volume, Std. Conditions	25.4751	2103.17	
Hardness (mg/L of Mg+2 and Ca+2)	608.264		

Notice that Brine volume decreased from 28 to approximately 25.54 m<sup>3</sup>/day, this is a 2.46 m<sup>3</sup>/day decrease. The roughly 2.46 tons of H<sub>2</sub>O mass partitioned to the vapor phase. This is because the produced gas analysis did not include the H<sub>2</sub>O fraction, and so material was missing from the gas analysis.

This 2.46 ton decrease equates to 136.13 kgmol of  $H_2O$ . Let's confirm the mass or mole transfer using the data in the reports and by manually calculating this transfer of water.

- ✓ In the **Phase Properties** table, record the moles of Vapor, i.e. 89201.3 kgmol/day
- ✓ Scroll down to the **Gas Composition** table
- ✓ Record the fraction of  $H_2O$  in the gas, i.e. ~0.153 mole%

Components	Gas (mole %)
C02	1.39748
H2O	0.152605
H2SO4	5.26566e-30
HCI	1.29904e-11
SO3	3.95339e-37
C2H6	1.99696
C3H8	0.798787

✓ Calculate the H₂O moles in Gas phase

 $Moles H_2O in Gas = \frac{0.152605 \,mol\%}{100\%} \times 89201.3 \,kgmol = 136.1256 \,kgmol$ 

Thus, we can see that saturating the hydrocarbon gas consumed ~136.5 kgmol. This represents the missing water mass or rather, the water unaccounted for in the gas analysis. *It needs to be added to the gas analysis so that the case is compute with no mass-balance error.* 

### Task 3b – Add the Missing Water

There are a few ways to saturate the gas with water:

- The first is to simply modify the gas analysis with ~0.153% H<sub>2</sub>O reported in the Saturator calculation
- The second is to saturate the gas with water using the Reconcile tab of the gas analysis
- The third is to create a makeup H2O stream that flows at 2.46 m<sup>3</sup>/day

This latter option is easy to rationalize, because the original gas analysis does not need to be modified, and using the makeup water approach reinforces the thrust of this exercise: conserving mass balance.

✓ Click on the Global Stream High GWR production object to expose all the objects in the Action pane



- ✓ Click on the Add Stream object to create a new stream Madd Stream
- ✓ Label it Makeup Water

The stream object is part of the Stream Analyzer software in OLI Studio. Its default settings are 1 kg water (55.508 moles) at 25°C and 1 bar.

Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5082
Temperature (°C)	25.0000
Pressure (atm)	1.00000
	(mol)
H2O	55.5082

We do not need to modify this at all. The default settings make it ideal as a makeup water stream. The mass is not what is desired, but this will be modified in the **Separator**.

- ✓ Click back on the Separator object ♣ ♣ Separator
- ✓ Go back to the **Design** tab
- ✓ In the Inlet tab, enter a third row, select: Whole Fluid, *Makeup water* and 2.46 m3/day

	Туре	Name	Flow
Г	Brine (m3/day)	Separator Water	28.0000
	Gas (std E3m3/day)	Produced Gas	2100.00
	Whole Fluid (m3/day)	Makeup water	2.46000

#### ✓ Calculate and go to the Report tab

✓ Review the (brine) volume in the **Phase Properties** table

Phase Properties				
Parameter	Liquid-1	Vapor		
pН	4.70607			
Mass (kg/day)	28063.4	1.57242e6		
Moles (True) (kgmol/day)	1550.51	89201.2		
Density (g/ml)	1.00183	0.0451143		
Specific Electrical Conductivity (µmho/cm)	24587.0			
Ionic Strength (x-based) (mol/mol)	3.59769e-3			
Ionic Strength (m-based) (mol/kg)	0.201238			
Viscosity, absolute (cP)	0.668673	0.0129268		
Thermal Conductivity (cal/hr m °C)	542.662	32.8227		
Volume Units	m3/day	E3m3/day		
Volume	28.0121	34.8542		
Volume, Std. Conditions Units	m3/day	std E3m3/day		
Volume, Std. Conditions	27.9388	2103.16		
Hardness (mg/L of Mg+2 and Ca+2)	554.636			

The volume is now 28.01 m3/day (exiting the separator). This value is now consistent with the reported production rates.

✓ Scroll down, and review the **Gas composition** table– specifically the H<sub>2</sub>O composition

Gas Composition			
Components	Gas (mole %)		
C02	1.39744		
H2O	0.152691		

These water fraction now represent the equilibrium partitioning among the water and gas phase.

## Assume Mass is Conserved from the Separator to the Reservoir

The previous calculation closed the mass balance between the reported flows and the computed flows, at least for the water flow rate. It may also be necessary to close the mass balance for the gas and condensate rates, but for now we will limit this study to the water balance.



The next step is to close the mass balance from the separator back to the reservoir. If we assume that no mass is lost as the fluid travels from the reservoir to the separator, then there is no additional work needed.



So, for this case, the fluid mass (gas+oil+water+solid) exiting the reservoir equals the fluid mass entering and then exiting the separator. This may be a bad assumption, especially since it presumes that no scale builds up in the production line.

We will proceed by creating a second Saturator block. This block will represent the reservoir conditions and the mass from the separator will be sent to the reservoir, thereby closing the mass balance.

## Task 4 – Create a Reservoir Object and Input the Separator Fluid

- ✓ Add a Saturator object from the Action panel 基 Add Saturator
- ✓ Press the <F2> key or use the Description tab to rename it *Reservoir*
- ✓ In the **Design** tab > **Inlets** tab, select *Whole Fluid*, *Separator*, and <Automatic> flow

Make certain that you select Separator, and not Separator water

Туре	Name	Flow
Whole Fluid (m3/day)	Separator	<automatic> 🗸</automatic>

The Automatic flow means that 100% of the Separator mass is transferred to the Reservoir.

✓ Enter the reservoir **Conditions** of 205<sup>o</sup>C and 1380 bar

Conditions	Value
Temperature (°C)	205.000
Pressure (bar)	1380.00

✓ Click on the **Solids** tab and check the **Standard** solids box



#### ✓ Calculate

- ✓ Click on the **Report** and go to the **Phase Properties** table
- ✓ Check the (brine) **volume** (Liquid-1 column and confirm that the volumes are in m3/day)

Phase Properties					
Parameter	Liquid-1	Solid	Liquid-2		
pН	4.69507		0.0		
Mass (kg/day)	591.860	0.0250535	1.59989e6		
Moles (True) (kgmol/day)	26.0557	2.44234e-4	90725.7		
Density (g/ml)	1.60718	2.75651	0.318817		
Specific Electrical Conductivity (µmho/cm)	8.34456e6		0.0		
Ionic Strength (x-based) (mol/mol)	0.212331		0.0		
Ionic Strength (m-based) (mol/kg)	19.0939		0.0		
Viscosity, absolute (cP)	54.3132		0.0737546		
Thermal Conductivity (cal/hr m °C)	550.321		232.621		
Volume (m3/day)	0.368261	9.08883e-6	5018.21		
Volume, Std. Conditions Units	m3/day		std m3/day		
Volume, Std. Conditions	0.403857		13538.5		
Hardness (mg/L of Mg+2 and Ca+2)	40553.8				

The brine volume at reservoir conditions is ~0.37 m3/day. This is a ~75% volume reduction (from 28 to 0.37 m3/day) (results may differ depending on version).

The remaining amount of water (i.e. 27.63 m3/day) shifted to the oil phase. This is due to the change in T/P conditions. The result of this mass transfer is a reservoir water composition that differs dramatically from the water sampled at the surface.

✓ Scroll down to the Brine Composition table

## ✓ Review the ions concentrations

Dring Composition

Dime Composition					
Cations	Value (mg/L)	Anions	Value (mg/L)	Neutrals	Value (mg/L)
K(+1)	2052.89	CI(-1)	4.97474e5	CO2	334.942
Na(+1)	2.73719e5	HCO3- (*)	2701.78	N2	12.6724
Ba(+2)	119.950	SO4-2	113.016	B(OH)3	1009.50
Ca(+2)	41792.1			C1	552.568
Fe(+2)	121.653			C2	19.0015
Mg(+2)	380.165			C3	5.00030
Sr(+2)	15.2066			nC4	0.795912
				C6	0.0847818
				C5	0.0607346
				iC5	1.87966
				iC4	0.702178

Notice, for example, that the Na<sup>+</sup> and Cl<sup>-</sup> concentrations are 76-times higher at reservoir conditions.

#### ✓ Scroll up to the Pre and Post Scaling Tendencies table

Formula	Mineral	Excess Solute	Excess Solute	Pre-Scale	Pre-Scale
		mg/L	lb/1000bbl	S, ST	SI, Index
Mg(OH)2	Brucite			9.40146e-3	-2.02680
NaCl	Halite	0.0	0.0	0.870639	-0.0601620
CaCO3	Calcite	65.1376	22.8311	1.03919	0.0166937
CaSO4.2H2O	Gypsum	0.0	0.0	0.0277308	-1.55704
CaSO4	Anhydrite	0.0	0.0	0.600394	-0.221564
KCI	sylvite			2.31430e-3	-2.63558
CaCl2.2H2O	Sinjarite			2.53792e-4	-3.59552
BaCO3	Witherite			4.10791e-4	-3.38638
BaSO4	Barite	2.89419	1.01443	1.02822	0.0120853
SrSO4	Celestine (celestite)	0.0	0.0	0.359126	-0.444753
SrCO3	Strontianite			0.0391057	-1.40776

#### Pre and Post Scaling Tendencies

Halite is near saturation, its saturation ratio (pre-scale value) is 0.87. Two other phases, CaCO<sub>3</sub> and BaSO<sub>4</sub> are computed as supersaturated, and their respective **Excess Solute in mg/L** are 65.14 and 2.89 respectively.

These reservoir results are, we think, representative of what enters the well. The next step is to study the fluid properties as it flows to the surface.

✓ Save the file

## Task 5 – Calculate the Scaling Scenario

The scaling scenario is run the same way as previous calculations. Enter the Reservoir whole fluid and test it at various T/P conditions.

- Add a Scaling Scenario from the Actions panel LAdd Scale Scenario
- ✓ Label it Production Conditions
- ✓ Select Whole Fluid, Reservoir, and <Automatic> flow

(s	Туре	Name	Flow
let	Whole Fluid (m3/day)	Reservoir	<automatic> 🗸</automatic>
	in all all		

- ✓ Click on the Conditions tab
- ✓ Enter the following conditions into the grid

Offshore Production Conditions				
Location	Temp (°C)	Press (bar)		
Reservoir	130	650		
Bottomhole	130	630		
SSSV	70	340		
Tubing head	65	320		
Choke	60	280		
Flowline	5	200		
Separator	40	60		

The grid should like the image below.



✓ Click on the **Solid** tab then select the **Standard** solids button



- ✓ Calculate or select the <F9> key
- Click on the Plot to review the Pre-scale tendencies



Four minerals are supersaturated: Calcite, Aragonite, Barite and Halite. Halite is slightly subsaturated at all conditions; we will investigate this later. Before this, we will confirm the computed and reported separator volumes (i.e., confirm earlier calculations).

✓ Click on the View Data button to review the data – View Data Variables
	Locations	CaCO3 (Calcite) - Sol Pre-scaling tendency	CaCO3 (Aragonite) - Sol Pre-scaling tendency	H2O - Sol Pre-scaling tendency	BaSO4 (Barite) - Sol Pre-scaling tendency	NaCl (Halite) - Sol Pre-scaling tendency
		Pre-ST	Pre-ST	Pre-ST	Pre-ST	Pre-ST
1	Reservoir	1.03919	0.948995	0.114485	1.02822	0.870639
2	Bottom hole	1.12208	1.02255	0.112917	1.08711	0.938461
3	SSSV	5.06790	4.26319	0.254459	0.0775714	0.0588402
4	Tubing Head	1.30578e-3	1.02831e-3	0.533975	0.0175966	3.60751e-4
5	Choke	1.16767e-3	9.12708e-4	0.558848	0.0201374	3.55984e-4
6	Flowline	9.67694e-4	7.44598e-4	0.613347	0.0274850	3.53470e-4
7	Separator	1.55065e-3	1.16572e-3	0.678478	0.0450825	3.86188e-4

The table shows two notable results. The first is that scale tendencies for Calcite, Aragonite and Barite increase across the perforations. The difference is small however, and so the risk may be equally low. The second is that be Halite saturation increases from S=0.87 to S=0.0.94 at *Bottomhole*. It remains sub-saturated, but this is a challenging question; is the measured concentration of Na+ and Cl- based on the reservoir composition, or is it possibly affected by salt buildup in the tubing? This question is beyond the scope of this course example, and will be taken up in a latter chapter.

✓ Click on the Variables button –

View Plot Variables

- ✓ Remove all the variables from the Y1-Axis
- ✓ Expand the **Phase Flow Properties** category. Add **Volume Liquid-1** to the Y1 Axis

ves	
- Phase Flow Properties	A X Axis
···· Mass - Liquid-1	>> Locations
···· Mass - Liquid-2	
Mass - Solid	V1 Avia
···· Mass - Total	Volume - Liquid 1
···· Mass - Vapor	Volume - Equid-1
···· Moles (Apparent) - Liquid-1	>>N
Moles (Apparent) - Liquid-2	
Moles (Apparent) - Total	<<
Moles (Inflow)	
Moles (True) - Liquid-1	
Moles (True) - Liquid-2	
Moles (True) - Solid	
Moles (True) - Total	Y2 Avia
Moles (True) - Vapor	1 2 AXIS
Volume - Liquid-2	
- Volume - Solid	
	V

✓ Click **OK** to view the plot (click on **View Plot** button if necessary)



The water flow changes significantly from the bottom to the top of the well – condensation is occurring somewhere within the tubing. Were additional depth conditions made available, then the condensation process could be refined further.

#### Summary

This is an example of a well that produces condensed water. This condensed water represents ~75% of the total water flow. As a result, the water sample obtained is diluted, and certain assumptions are made so that we were able to compute scale risks during production. The conclusion is that reservoir brine is close to NaCl saturation and supersaturated with Calcite, Aragonite, and Barite.

## Chapter 11 – Oil Well with Gas Lift

## Overview

This case is an oil well produced with the aid of gas lift. It is a two-zone production, with brine and oil produced at 2500m MD and a gas cap produced at 2450m MD. The gas lift valve (GLV) is about halfway up the well at 1200m MD. The process schematic is below. There are four inflow streams; brine, oil, gas cap gas, and lift gas. Calcite cementation is part of the rock matrix and this mineral is in equilibrium with the reservoir oil & brine.



This chapter has seven tasks. The first four are data entry and use ScaleChem objects brine, gas, and oil analyses. Task five is the reservoir saturation calculation and task six is the facilities calculation to model production. The final task is to evaluate results and make any modifications as needed. The first five tasks are similar to those used in previous chapters, which is expected, as the software is designed to work in this way.

✓ Save and close any cases currently on the screen

### Task 1 – Add the GLV Brine analysis

- ✓ Select File > New and Save as Chapter 11 Lift Gas Well
- ✓ Click on **Streams** and change the name to **Gas Lift Valve**

Navigator # * ×	🍓 Streams	
• Streams	Description	Object Map
	Name: High G	WR production

✓ Select Gas Lift Valve and go to Chemistry > Model Options...

File Edit Streams Calculati	ons	Chemistry	Tools	View	Wind
🗄 D 🚅 🖬   X 🖻 🖻   🍜 🖇	2 🕅	Pre-bu	uilt Mod	els	> x
Navigator a • ×	4.6	Templ	ates		>
SSC Basics - Chapter 11 - Lift G:	De	Mode	Option	s	

✓ Under the Databanks tab select the MSE-SRK (H3O+ ion) as the Thermodynamic Framework, and click OK.

Databanks	Redox	Phases	T/P Span					
Databanks								
	Thermodynamic Framework							
MSE-SRK (H3O+ ion) V								

- ✓ Label it GLV Brine
- ✓ Enter the ions from the table below in the **Data** Entry grid

GLV Brine Analysis								
Cations mg/l Anions mg/l Neutrals mg/l Measured Data								
Na+1	26500	CI-1	43150	SiO2	26	Temperature (°C)	15	
K+1	350	SO4-2	20	B(OH)3	60	Pressure (atm)	1	
Ca+2	800	C2H3O2-1	30			pН	7.2	
Mg+2	170					Alkalinity	140	
Sr+2	120					TDS, mg/L	42000	
Ba+2	60							

✓ After entering the data in the Data Entry tab, select the Show Non-zero Only option and keep the default balance option as Dominant Ion

The screen should look like the image below

<u>ک</u>	Variable	Value	Balanced	Entry Options		
E I	Cation	is (mg/L)		Units		
a	Na+1	26500.0	26500.0	ma/l ×		
Dat	K+1	350.000	350.000	Display		
	Ca+2	800.000	800.000			
	Mg+2	170.000	170.000	Formula		
cie	Sr+2	120.000	120.000	Show Non-zero Only		
U U	Ba+2	60.0000	60.0000	Show Balanced Column		
Å						
	Anion	s (mg/L)		i emplate Manager		
	CI-1	43150.0	43189.8	Standard 🗸		
	S04-2	20.0000	20.0000			
	C2H3O2-1	30.0000	30.0000	Save as		
	Neutra	Neutrals (mg/L)				
	B(OH)3	60.0000	60.0000	Туре		
	Si02	26.0000	26.0000	Dominant Ion		
				Commune ton		

- ✓ Select the **Reconcile** (blue) tab and enter the Measured Data from the above table (15°C, 1 atm, 7.2 pH, 140 mg HCO3/L alkalinity, and 42000 TDS)
- ✓ Select the Measured pH and Alkalinity option
- 1 The Alkalinity (titration) End Point pH is set to 4.5. Keep this value

#### ✓ Calculate

oncile Data Entry	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 🥥			
Sec		Properties	Measured	Calculated		
( <b>"</b>	L	Temperature (°C)	15.0000			
		Pressure (atm)	1.00000			
		рН	7.20000	7.20000		
	Г	Alkalinity (mg HCO3/L)	140.000	140.000		
	Г	Alkalinity End Point pH	4.50000			
	Г	Density (g/ml)	0.0	1.04969		
	Г	Elec Cond, specific (µmho/cm)	0.0	80356.9		
	Г	Total Dissolved Solids (mg/L)	42000.0	N/A		
		Comp	osition Adjustments			
	Г	Added titrant (mg/L) HCI		-74.3595		
		Add carbonate (mg/L CO2)		95.2259		
		Add Charge Balance (mg/L CI-1)		39.8325		

## Task 2 – Add the Gas Cap Analysis

- ✓ Add a new Gas Analysis <sup>⊕</sup> Add Gas Analysis
- ✓ Label it Gas Cap –
   ✓ Streams GLV Brine Gas Cap
- ✓ Select the **Expanded** template –

Template Manager	
Expanded	

✓ Enter the following composition:

Gas	Cap Analysis Composi	ition
Formula	Component name	Mole %
H2O	Water	0
CH4	Methane	90
N2	Nitrogen	2.1
CO2	Carbon dioxide	1.33
C2H6	Ethane	2.37
C3H8	Propane	1.25
i-C4H10	Isobutane	0.46
n-C4H10	n-Butane	0.59
i-C5H12	Isopentane	0.32
C5H12	n-Pentane	0.34
C6H14	n-Hexane	0.44
C7H16	n-Heptane	0.36
C9H20	n-Nonane	0.11
C10H22	n-Decane	0.09
C11H24	n-Undecane	0.07
C12H26	Dodecane	0.03
C13H28	n-Tridecane	0.02
C14H30	n-Tetradecane	0.02
C15H32	n-Pentadecane	0.01
C16H34	n-Hexadecane	0.01
C6H6	Benzene	0.01
C7H8	Toluene	0.02
C8H10	Ethylbenzene	0.02
C8H10	1,3-Dimethylbenzene	0.02
C8H10	o-Xylene	0.01

There is no water present in the gas, and it is reasonable to add it. However, since the production has a high-water rate, the additional water will be negligible to the brine mass.

	Component	Value	Normalized	Entry Options
Г		Subtotal: 1	Subtotal: 100.	Units
	Water	0.0	0.0	mole % 🗸 🗸
	Methane	90.0000	90.0000	Display
	Nitrogen	2.10000	2.10000	Display Name V
	Carbon dioxide	1.33000	1.33000	
	Ethane	2.37000	2.37000	Show Non-zero Only
Γ	Propane	1.25000	1.25000	Show Normalized Column
	Isobutane	0.460000	0.460000	Template Manager
	n-Butane	0.590000	0.590000	· · · · · · · · · · · · · · · · · · ·
	Isopentane	0.320000	0.320000	Expanded $\vee$
	n-Pentane	0.340000	0.340000	Save as
	n-Hexane	0.440000	0.440000	
	n-Heptane	0.360000	0.360000	
Γ	n-Nonane	0.110000	0.110000	Normalize Options
	n-Decane	0.0900000	0.0900000	Makeup 🗸 🗸
	n-Undecane	0.0700000	0.0700000	Group Manager
	Dodecane	0.0300000	0.0300000	
	n-Tridecane	0.0200000	0.0200000	OSE Groups Add
	n-Tetradecane	0.0200000	0.0200000	
	n-Pentadecane	0.0100000	0.0100000	
	n-Hexadecane	0.0100000	0.0100000	
	Benzene	0.0100000	0.0100000	
	Toluene	0.0200000	0.0200000	
	Ethylbenzene	0.0200000	0.0200000	
	1,3-Dimethylbenzen	0.0200000	0.0200000	
	o-Xylene	0.0100000	0.0100000	

Gas Cap in Display Name view

## Task 3 – Add the GLV Oil (Reservoir Oil)

- Add an Oil Analysis Add Oil Analysis
- ✓ Label it GLV Oil
- ✓ Input the following data in the **Combined** tab; switch between Formula and Display view

GLV Oil Analysis Composition								
Formula	Component name	Mole %		Formula	Component name	Mole %		
H2O	Water	0		C18H38	n-Octadecane	1.29		
CH4	Methane	38.67		C19H40	n-Nonadecane	1.19		
C2H6	Ethane	3.38		C20H42	n-Eicosane	0.91		
C3H8	Propane	3.11		C21H44	Heneicosane	0.82		
i-C4H10	Isobutane	2.66		C22H46	Docosane	0.74		
n-C4H10	n-Butane	2.44		C23H48	Tricosane	0.67		
i-C5H12	Isopentane	2.02		C24H50	n-Tetracosane	0.57		
C5H12	n-Pentane	1.57		C25H52	Pentacosane	0.5		
C6H14	n-Hexane	3.24		N2	Nitrogen	1.5		
C7H16	n-Heptane	3.7		CO2	Carbon dioxide	1.19		
n-C8H18	n-Octane	2.87		C6H6	Benzene	0.08		
C9H20	n-Nonane	2.45		C7H8	Toluene	0.37		
C10H22	n-Decane	2.8		C8H10	Ethylbenzene	0.34		
C11H24	n-Undecane	2.63		C8H10	1,3-Dimethylbenzene	0.65		
C12H26	Dodecane	2.36		C8H10	o-Xylene	0.29		
C13H28	n-Tridecane	2.33						
C14H30	n-Tetradecane	1.86						
C15H32	n-Pentadecane	1.86		Pseudocomponent (next step)		p)		
C16H34	n-Hexadecane	1.49		C30PLUS	PseudoC30	6.15		
C17H36	n-Heptadecane	1.3			nBP=476 MW= 394			

- ✓ Select the **Pseduocomponents** tab
- ✓ Type the **Component** name as C30PLUS then press <Enter>
- ✓ Enter the Molecular Weight of 394 g/mole
- ✓ Enter the Normal Boiling Point of 476 °C
- ✓ Give it a **Value** of 6.15 mole%

Component	Molecular Weight	Nomal Boiling Point (°C)	Specific Gravity	Thermo Method	Value (mole %)	
C30PLUS	394.000	476.000		API-8	6.15000	

✓ Go back to the **Combined** tab and check if the Pseudocomponent registered

<b>D</b>	Component	Value	Normalized
oine	Inflows	Subtotal: 93.8500/100.000 (mole %)	Subtotal: 93.8500/100.000 (mole %)
dm	Water	0.0	0.0
ပိ	Methane	38.6700	38.6700
	Ethane	3.38000	3.38000
	Propane	3.11000	3.11000
nts	Isobutane	2.66000	2.66000
one	n-Butane	2.44000	2.44000
du	Isopentane	2.02000	2.02000
000	n-Pentane	1.57000	1.57000
opne	n-Hexane	3.24000	3.24000
Pse	n-Heptane	3.70000	3.70000
	n-Octane	2.87000	2.87000
	n-Nonane	2.45000	2.45000
(es	n-Decane	2.80000	2.80000
As	n-Undecane	2.63000	2.63000
	Dodecane	2.36000	2.36000
e	n-Tridecane	2.33000	2.33000
nci	n-Tetradecane	1.86000	1.86000
e C o	n-Pentadecane	1.86000	1.86000
Ř	n-Hexadecane	1.49000	1.49000
	n-Heptadecane	1.30000	1.30000
	n-Octadecane	1.29000	1.29000
	n-Nonadecane	1.19000	1.19000
	n-Eicosane	0.910000	0.910000
	Heneicosane	0.820000	0.820000
	Docosane	0.740000	0.740000
	Tricosane	0.670000	0.670000
	n-Tetracosane	0.570000	0.570000
	Pentacosane	0.500000	0.500000
	Nitrogen	1.50000	1.50000
	Carbon dioxide	1.19000	1.19000
	Benzene	0.080000	0.0800000
	Toluene	0.370000	0.370000
	Ethylbenzene	0.340000	0.340000
	1,3-Dimethylbenzene	0.650000	0.650000
	o-Xylene	0.290000	0.290000
	Pseudocomponents	Subtotal: 6.15000/100.000 (mole %)	Subtotal: 6.15000/100.000 (mole %)
	C30PLUS	6.15000	6.15000

You will not use the reconcile step here either. Again, the brine mass is high relative to the oil, and therefore the small amount of  $H_2O$  in the oil phase is small relative to the total brine mass. Not taking this step adds a small amount of error to the calculation, but this is less than 1%.

#### Task 4 – Add the Lift Gas Analysis

Lift gas may exist as sales gas or come from a separate source. In this case, the lift gas is similar but not identical to the separator gas. This means that the lift gas is a mixture of production gases from the field.

- ✓ Add a new Gas Analysis <sup>⊕</sup> Add Gas Analysis
- ✓ Label it *Lift Gas*

Template Manager

- Select the Expanded template –
- ✓ Enter the following gas composition:

Lift Gas Composition				
Formula	Component Name	Lift Gas		
H2O	Water	0		
N2	Nitrogen	1.9		
CO2	Carbon dioxide	0.75		
CH4	Methane	81.35		
C2H6	Ethane	7.2		
C3H8	Propane	4.87		
i-C4H10	Isobutane	0.85		
n-C4H10	n-Butane	1.71		
i-C5H12	Isopentane	0.4		
C5H12	n-Pentane	0.21		
C6H14	n-Hexane	0.13		

✓ Check the Show Non-zero Only box

Component	Value	Normalized	Entry Options
	Subtotal: 99.37	Subtotal: 100.000/	Units
H2O	0.0	0.0	mole % 🗸 🗸
N2	1.90000	1.90000	Display
CO2	0.750000	0.750000	Formula
CH4	81.3500	81.9800	
C2H6	7.20000	7.20000	Show Non-zero Only
C3H8	4.87000	4.87000	Show Normalized Column
i-C4H10	0.850000	0.850000	Template Manager
n-C4H10	1.71000	1.71000	
i-C5H12	0.400000	0.400000	Standard $\checkmark$
C5H12	0.210000	0.210000	Save as
C6H14	0.130000	0.130000	

This gas analysis is also missing the water content. You will not use the H2O saturation option to calculate the amount. This step is being ignored purposely to illustrate that the water saturation option although improving mass balance, does not necessarily affect the final results, even though the water cut is 10 % v/v.

## Task 5 – Add the GLV-Reservoir (Saturator)

The oil and brine are at equilibrium in the reservoir. This equilibrium will be set using the Saturator object. You will set the saturator to equilibrate the gas and oil at reservoir conditions, and to saturate the mixture with calcite (the reservoir's cement mineral).

- Add a Saturator Add Saturator
- ✓ Label it GLV Reservoir
- ✓ Enter **Brine** type, select **GLV Brine**, and 296 m³/day flow
- ✓ Enter Oil type, select GLV Oil, and 1000 std m3/day in the next row
- ✓ Enter the Reservoir **Conditions** of 137°C and 170 atm

ets		Туре	Name	Flow
Ξ		Brine (m3/day)	GLV Brine	296.000
		Oil (std m3/day)	GLV Oil	1000.00
-		<select></select>		
Soli				
	Г	Co	nditions	Value
		Temperature (°C)		137.000
		Pressure (bar)		170.000

✓ Select the **Standard** box in the **Solid** tab

id Selection (check solids allowed to form)			
	BaSO4 (Barite)		
	CaCO3 (Calcite)		
	CaSO4 (Anhydrite)		
	CaSO4.2H2O (Gypsum)		
	MaCl (Halite)		
	SrSO4 (Celestine (celestite))		
	🗄 🗹 Expanded		

✓ Calculate

DI D ()

- ✓ Select the **Report** tab
- ✓ Go to the **Phase Properties** table and review the Liquid-1 volume (at std conditions)

mase Properties					
Parameter	Liquid-1	Vapor	Liquid-2		
Volume Units	m3/day	E3m3/day	m3/day		
Volume	312.234	0.0688810	1447.74		
Volume, Std. Conditions Units	m3/day	std E3m3/day	std m3/day		
Volume, Std. Conditions	294.289	8.73629	1277.60		

The input water rate is 296 m3/day. The computed rate (at standard conditions – no thermal expansion) is 294.29 m3/day, a 0.6% decrease. Had the oil been saturated with water at reservoir conditions, this difference would have been eliminated.

✓ Scroll down to the Pre and Post Scale Tendencies table

Pre and Post Scaling Tendencies							
Formula	Mineral	Excess Solute	Excess Solute	Pre-Scale	Pre-Scale		
		mg/L	lb/1000bbl	S, ST	SI, Index		
SiO2	lechatelierite			0.0383142	-1.41664		
BaCO3	Witherite			9.16279e-4	-3.03797		
Mg(OH)2	Brucite			3.56495e-4	-3.44795		
NaCl	Halite	0.0	0.0	0.0149022	-1.82675		
BaSO4	Barite	0.0	0.0	0.961609	-0.0170017		
SrSO4	Celestine (celestite)	0.0	0.0	0.0408019	-1.38932		
SrCO3	Strontianite			0.0276255	-1.55869		
CaCO3	Calcite	0.0	0.0	0.188042	-0.725745		
CaSO4.2H2O	Gypsum	0.0	0.0	3.48472e-3	-2.45783		
CaSO4	Anhydrite	0.0	0.0	0.0173395	-1.76096		
KCI	sylvite			1.18096e-4	-3.92777		

Barite is nearly saturated with a value of 0.96, and no excess solute is computed to precipitate. It is reasonable to consider saturating the fluid with barite; however, we will not saturate it since the focus on the next step is to develop the **Facilities** calculation to model the flow conditions.

#### ✓ Save the file

#### Task 6a – Add the Well Production (Facilities)

The last, and primary task of this chapter is to use the **Facilities** object to model production from the two reservoirs through the gas life up to the surface facilities. Since the flow dynamic is more complicated than the Scale Scenario can handle, the Facilities object is required. The image below is the process flow diagram.





Material enters the well at three locations; brine and oil enter at 2500m MD, the gas cap gas enters at 2450m MD and lift gas is enters at 1200m MD. Material also exits at three locations, Gas to Sales, Oil Separator and Brine to disposal.

The specifications for the flow diagram is provided in the table below. It is divided into three sections, the conditions, inflows, and additional specifications (notes). You will enter the information in that order.

	Descriptions of GLV Production Nodes in Facilities Calculation								
	Node Conditio			Inflows					
Node	Node Name	T (°C)	P (bar)	Type(s)	Inlet Name(s)	Flow(s)			
1	Reservoir	137	170	Whole Fluid	GLV Reservoir	Automatic			
2	2500m MD	137	170	Whole Fluid from	Reservoir	Automatic			
	0.450 145	405	450	Whole fluid from	2500m MD	Calculated			
3	2450m MD	135	152	Gas	Gas Cap	5 std E3m3/d			
4	1250m MD before GLV	115	120	Whole fluid from	2450m MD	Calculated			
5	1200m MD GLV exit	1200m MD	1200m MD 101	101	101 105	Whole fluid from	1250m MD before GLV	Calculated	Drop
				Gas	Lift Gas	30 std E3m3/d	SOlids		
6	Wellhead	80	70	Whole fluid from	1200m MD GLV exit	Calculated			
7	Gas Separator	40	30	Whole fluid from	Wellhead	Calculated	Drop solids		
8	Oil Separator	70	15	Oil from	Gas Separator	Calculated	Drop solids		
		4.5		Gas from	Gas Separator	Calculated			
9	Gas to Sales	15	1	Gas from	Oil Separator	Calculated			
10	Brine to	4.5		Brine from	Gas Separator	Calculated			
10	Disposal	15	1	Brine from	Oil Separator	Calculated			

- ✓ Add a Facilities object <sup>♣</sup>t Add Facilities
- ✓ Label it GLV Production



- $\checkmark$  Add ten nodes total (press the Add button 9 times) –
- ✓ Label each node using the table above
- ✓ Go to the Conditions (blue) tab to enter the Temperature and Pressure conditions at each location

The screen should look like the image below.

ecs		Node #	Name	Temperature (°C)	Pressure (bar)
5 S		1	Reservoir	137.000	170.000
low		2	2500 m MD	137.000	170.000
Ē		3	2450m MD	135.000	152.000
		4	1250m MD before GL	115.000	120.000
s		5	1200 m MD GLV Exit	101.000	105.000
tio		6	Wellhead	80.0000	70.0000
ipi		7	Gas Separator	40.0000	30.0000
0 C		8	Oil Separator	70.0000	15.0000
		9	Gas to Sales	15.0000	1.00000
		10	Brine to Disposal	15.0000	1.00000

✓ Go back to the Inflow Specs tab and start connecting the inflows, according to the table <u>above</u>

The oil and brine are at equilibrium in the reservoir (2500m MD). By comparison, the gas cap is not in contact with the water and so it enters at a different depth, and a different node (2450m MD). The screen should look like the image below when all nodes are added and connected with their respective inflows.



• Note, that three nodes contain two inflows, for example the entry for the **2450 m MD** node looks like the image below.

	Co	Value		
	Temperature (°C)	135.0		
	Pressure (bar)	152.0		
	Туре	Name	Flow	
Г	Whole Fluid from (m3/day)	2500 m MD	Calculated	
	Gas (std E3m3/day)	Gas Cap	5,0000	

Inflows for Node 3, 2450m MD

✓ Select the **Solid** tab and check the **Standard** Solids box



- ✓ Save the file
- ✓ Calculate

## Task 6b – Studying the Facilities plot/report and making modifications to the calculations

The focus of this section is to review plot. The items to be reviewed include:

- 1. Surface flow rates Do the calculations match the volumes measured for each phase?
- 2. **Brine Analysis** Do the calculated concentrations at the sampling location match the values measured in the actual sample?
- ✓ Select the Plot tab

The default plot is the Dominant Pre-Scaling Tendencies vs Locations



Notice that Barite is predicted to be at near saturation at reservoir conditions. As the fluid moves to the different facilities locations the risk of scaling increases.

- ✓ Press the Variables button
- ✓ Remove the Variables in the Y1 axis
- ✓ Expand the Phase Flow Properties category

Let's find out if the calculations match the volumes measured for each phase

- ✓ Select the following variables:
  - Volume, Std. Conditions Vapor
  - Volume, Std. Conditions –Liquid-2
  - Volume Liquid-1

Curves	
Phase Flow Properties	× Axis
Mass - Liquid-1	>> Nodes
Mass - Liquid-2	
Mass - Total	Y1 Avie
···· Mass - Vapor	Volume_Std_Conditions - Vanor
Moles (Apparent) - Liquid-1	Volume, Std. Conditions - Liquid-2
Moles (Apparent) - Liquid-2	Notice, state conditions Equid 2
Molee (Apparent) - Total	

#### ✓ Press **OK** then select the **View Data** button

	Nodes	Volume, Std. Conditions - Vapor	Volume, Std. Conditions - Liquid-2	Volume, Std. Conditions - Liquid-1	Volume - Vapor	Volume - Liquid-2	Volume - Liquid-1
	?	std E3m3/day	std m3/day	m3/day	E3m3/day	m3/day	m3/day
1	Reservoir	8.73629	1277.60	294.289	0.0688810	1447.74	312.234
2	2500 m MD	8.73629	1277.60	294.289	0.0688810	1447.74	312.234
3	2450 m MD	27.0618	1242.19	294.126	0.236684	1403.96	311.816
4	1250 m MD b	43.3950	1197.99	295.243	0.453093	1319.11	308.712
5	1200 m MD G	78.2639	1185.66	295.574	0.893110	1284.26	306.232
6	Wellhead	94.5933	1145.44	296.201	1.53836	1212.25	303.231
7	Gas Separat	111.366	1106.29	296.865	3.84781	1127.64	298.236
8	Oil Separator	13.2111	1072.88		1.02781	1122.60	0.0
9	Gas to Sales	124.580	2.13147e-4		126.282	2.13148e-4	0.0
10	Brine to Disp	0.158495		296.654	0.160661	0.0	295.717

Now, let's check if the calculated concentrations at the sampling location match the values measured in the actual sample.

- ✓ Select the Variables button and remove all the variables from the Y1 Axis
- ✓ Expand MBG Totals Liquid-1 and double-click Ba(+2) Liq 1, Ca+2 Liq 1, Cl(-1) Liq 1, and S(+6) Liq 1

Curves		
MBG Totals - Liquid-1     Oominant MBG Totals - Liquid-1     ACETATEION Liq1     - B(+3) Liq1     - B(+2ENE Liq1     - C(+4) Liq1	<b>^</b>	X Axis Nodes S(+6) Liq1
	>>	Ca(+2) Liq1 Ba(+2) Liq1

✓ Press **OK** and view the table

	Nodes	S(+6) Liq1	Cl(-1) Liq1	Ca(+2) Liq1	Ba(+2) Liq1
	?	mg/L	mg/L	mg/L	mg/L
1	Reservoir	6.32888	40875.7	758.404	56.8803
2	2500 m MD	6.32888	40875.7	758.404	56.8803
3	2450 m MD	6.33739	40930.6	759.423	56.9567
4	1250 m MD before GLV	6.40110	41342.1	767.059	57.5294
5	1200 m MD GLV exit	6.45294	41676.9	773.270	57.9953
6	Wellhead	6.51679	42089.3	780.922	58.5691
7	Gas Separator	6.62595	42794.3	794.003	59.5502
8	Oil Separator	0.0	0.0	0.0	0.0
9	Gas to Sales	0.0	0.0	0.0	0.0
10	Brine to Disposal	6.68238	43158.7	800.764	60.0573

## Summary

This chapter introduced another approach to using the **Facilities** object.

# Chapter 12 – Calculating Alkalinity

## **Overview**

In this chapter you will learn:

- How to calculate acid:anion ratios at varying ionic strengths
- Use the Mixing Water calculation as a pH titration apparatus
- Understand how weak acid chemistry affects alkalinity
- Compare true bicarbonate and carbonate concentrations to carbonate alkalinity

## Investigating the Components that Create Alkalinity

The alkalinity measurement is used to compute carbonate scale tendencies and pH buffer capacity. Bicarbonate, and to a lesser degree, borates, organic acids and bisulfides, provide alkalinity to produced water. Therefore, this chapter is an introduction to quantifying alkalinity beyond the standard contributions from  $HCO_3^-$ ,  $CO_3^{-2}$  and  $OH^-$ .

#### Carbonate Alkalinity Contributions

The Standard Methods for the Examination of Water and Wastewater codified the measurements to determine alkalinity. In its second edition (1912), the book linked alkalinity and total hardness to CaCO<sub>3</sub> scale (an interesting side note, in the year of publication, olive oil-derived castile soap was used to measure total water hardness instead of inductively coupled plasma spectrometry). Measurements related to Lacmoid, Erythrosine, Methyl orange, silver nitrate and phenolphthalein, were all designed to measure carbonate and hydroxide alkalinity. The contribution of non-carbonate and non-hydroxide buffers, like organic acids, do not have supporting text. Oilfield water analyses continue to use the original experimental design with the same endpoint, despite the measurement does not capture the produced water species complexity.

Alkalinity equations are a series of chemical reactions with measurable endpoints, described below:

 $HCO_3^{-2} + H^+ = CO_2 + H_2O$  considerd complete by pH < 4.5 (25°C)  $CO_3^{-2} + H^+ = HCO_3^-$  considerd complete by pH < 8.5 (25°C)  $OH^- + H^+ = H_2O$  considerd complete by pH < 10 (25°C) Thus, a simple definition for carbonate alkalinity is:

Carbonate Alkalinity = Total  $H^+$  required to convert all  $CO_3^{-2}$ ,  $HCO_3^-$ , and  $OH^-$  to  $CO_2$ =  $H^+$  (from  $CO_3^{-2}$ ) +  $H^+$  (from  $HCO_3^-$  and neutralized  $CO_3^{-2}$ ) +  $H^+$  (from  $OH^-$ ) = total acid added to bring the pH to < 4.5

$$= 2CO_3^{-2} + HCO_3^{-} + OH^{-1}$$

Lastly, a mass balance equation for carbonate:

$$Carbonate_{Total} = HCO_3^- + CO_3^{-2}$$

A Bjerrum plot, in which carbonate concentration is fixed, shows the relative concentration of each species as functions of pH (also shown is the relative OH<sup>-</sup> concentration):



pH - Aqueous [pH]

The calculations provide measurable hydroxide, carbonate and bicarbonate concentrations at a relative pH: free hydroxide (OH-) exists above 10 pH; carbonate exists above 8.5 pH; and bicarbonate exists between 4.5 and 8.5 pH.

An alkalinity titration procedure is as follows:

- 1. Start with a known sample volume
- 2. Add two indicators the first activates at 8.5 pH or higher and the second is active below 4.5 pH
- 3. Titrate the sample with a strong acid of known composition

When the first indicator deactivates (the pH drops below 8.5), the amount of titrant added is the carbonate alkalinity and hydroxide alkalinity point. The following equation converts the acid volume to the carbonate alkalinity.

$$CO_{3}^{-} Alk\left(\frac{mg}{L}\right) as HCO_{3}^{-}$$

$$= Acid volume used to 8.5 pH(L) \times Acid Conc.\left(\frac{moles}{L}\right) \times 61020 \left(\frac{mg HCO_{3}^{-}}{mole}\right)$$

$$\times \frac{1}{Sample Vol(L)}$$

4. The sample is titrated further until it until the second indicator appears (pH<4.5). This is the bicarbonate alkalinity endpoint. This information is used as follows:

$$\begin{aligned} HCO_{3}^{-} Alk\left(\frac{mg}{L}\right) & as \ HCO_{3}^{-} \\ &= Vol \ Acid \ for \ Bicarbonate \ Alk \ Titration \ (L) \times Acid \ Conc. \left(\frac{moles}{L}\right) \\ &\times 61020 \ \left(\frac{mg \ HCO_{3}^{-}}{mole}\right) \times \frac{1}{Sample \ Vol \ (L)} \end{aligned}$$

The two titrations combine to calculate the total alkalinity

$$Total Alk\left(\frac{mg}{L}\right) as HCO_{3}^{-}$$

$$= Vol Acid for Carbonate Alk Titration (L)$$

$$+ Vol Acid for Biarbonate Alk Titration (L) \times Acid Conc.\left(\frac{moles}{L}\right)$$

$$\times 61020\left(\frac{mg HCO_{3}^{-}}{mole}\right) \times \frac{1}{Sample Vol (L)}$$

$$OH^{-}Alk\left(\frac{mg}{L}\right) as HCO_{3}^{-} = CO_{3}^{-}Alk\left(\frac{mg}{L}\right) - HCO_{3}^{-}Alk\left(\frac{mg}{L}\right)$$

 In the absence of carbonates or in addition to carbonate, the OH<sup>-</sup> alkalinity can also be determined from the difference between the carbonate and bicarbonate alkalinity and is only relevant above 9.5 or 10pH (OH<sup>-</sup>>10<sup>-4.5</sup> M or ~0.5ppm).

$$Alk_{OH} = 2 * Alk_{8.5pH EP} - Alk_{4.5pH EP}$$

If the value is negative, then there is no hydroxide alkalinity. Hydroxide alkalinity is not common in production waters because the pH is never that high. It is present in drilling and alkaline injection fluids.

#### **Problem Statement**

Oilfield waters do not conform chemically, to the fresh water used in the original alkalinity method. Organic acids, borates, phosphates, sulfides and other proton-accepting species produce alkalinity. Consequently, the standard alkalinity titration cannot be used to measure the bicarbonate/carbonate concentration. We will evaluate this in the following examples.

#### Task 1: Quantifying Alkalinity of Certain Anions

You will compute the alkalinity of 100 mg/L of the following anions:  $HCO_3^-$ ,  $CO_3^{-2}$ ,  $OH^-$ ,  $CH_3CO_2^-$ ,  $B(OH)_4^-$ ,  $SO_4^{-2}$ ,  $CI^-$  and HS. The counter-ion will be sodium making the system basic. There will be no additional salt (salinity) added the first set of calculations. This will allow you to quantify alkalinity at near-ideal activities. You will calculate a second time in the presence of 1M NaCl. You will conclude this section by producing a quantitative table showing the contribution to alkalinity as a function of species and salinity.

We will be using °C and atm units for Temperature and Pressure so please adjust accordingly.

- ✓ Create a new file called "Alkalinity"
- ✓ Add a new brine analysis
- ✓ Rename it *Alkalinity*

SSC B	asics - Chapter 20 - Alkal			
🍓 Str	🍓 Streams			
<b>)</b>	Alkalinity			

#### Bicarbonate

- ✓ Select the **Design** tab
- ✓ Find HCO3-1 in the Anions grid and give it a value of 100 mg/L
- ✓ Check the **Non-zero only** box

Variable	Value	Balanced	Entry Options
Cations (n	ng/L)		Units
Na+1	0.0	37.6778	mg/L ~
			Display
Anions (n	ng/L)		E-maile and
HCO3-1	100.000	100.000	Formula
			Show Non-zero Only

- ✓ Select the **Reconcile** tab
- ✓ Leave the default reconciliation option (Concentration Data Only)
- ✓ Click **calculate** and document the pH and alkalinity

Properties	Measured	Calculated
Temperature (°C)	25.0000	
Pressure (atm)	1.00000	
рН	0.0	8.26888
Alkalinity (mg HCO3/L)	0.0	100.660
Density (g/ml)	0.0	0.997086
Elec Cond, specific (µmho/cm)	0.0	150.960
Total Dissolved Solids (mg/L)	0.0	N/A
Compo	sition Adjustments	
Add Charge Balance (mg/L Na+1)		37.6778

The calculated pH is 8.27. The calculated alkalinity is 100.7 mg/L and is entirely the bicarbonate alkalinity. The 0.7 mg/L addition to the alkalinity value is due to the pH endpoint and minor activity coefficient effects.

The next three steps will make it easier for us to perform titrations later. Alternatively, we can continue working in the same *Alkalinity* file and replace the anions as we go along. Subsequent instructions will be applicable for both approaches.

✓ In the Navigator pane, right-mouse click *Alkalinity* and press copy



Right-mouse click the Streams icon, then select paste. Repeat this 7 times, to create a total of 8 objects in the navigator panel.

<b>▲</b> Stree	ume.	Descri
	Arrange	>
	Cut	
	Сору	
	Paste	

The software designates the new streams as Alkalinity -1, Alkalinity-2, and so on.

✓ Rename the objects so that the anion they contain will be easily identifiable: Alkalinity-Bicarbonate, Alkalinity-Carbonate, Alkalinity-Hydroxide, Alkalinity-Acetate, Alkalinity-Borate, Alkalinity-Sulfate, Alkalinity-Chloride, and Alkalinity-Bisulfide



#### Carbonate

- ✓ Select the Alkalinity-Carbonate brine analysis stream
- ✓ Remove the 100 mg/L HCO3-1 and add 100 mg/L CO3-2
- ✓ Check the Non-zero only box

Cations	(mg/L)		
Ma+1			Units
2 ·····	0.0	76.6214	mg/L 🗸
Da			Display
Anions	mg/L)		Earmula
C03-2	100.000	100.000	
g			Show Non-zero Only
Neutrals	(mg/L)		Show Balanced Column
U U			

• You can either type in CO3-2 in an empty cell, or select the **Expanded Template** to locate it in the Anion grid.

✓ Select the **Reconcile** tab and recalculate

Properties	Measured	Calculated
Temperature (°C)	25.0000	
Pressure (atm)	1.00000	
рН	0.0	10.6347
Alkalinity (mg HCO3/L)	0.0	204.114
Density (g/ml)	0.0	0.997171
Elec Cond, specific (µmho/cm)	0.0	431.288
Total Dissolved Solids (mg/L)	0.0	N/A
Compo	sition Adjustments	
Add Charge Balance (mg/L Na+1)		76.6214

The alkalinity is 204.1 mg/L as  $HCO_3^-$  twice the  $CO_3^{-2}$  concentration added, and is consistent with the above equation. The  $HCO_3^-$  formula weight is 61.02 g/mole and  $CO_3^{-2}$  is 60.01 g/mole – a mole ratio of 1.7%. Two factors contribute to the alkalinity increase. The first is that  $CO_3^{-2}$  accepts two  $H^+$  ions one above 8.5 pH and one above 4.5 pH. The second is that 1.7% additional moles of carbonate are added because of the weight difference. Thus, the theoretical alkalinity of 100 mg/L alkalinity as  $HCO_3^-$  \*2 \* 1.7% = 203.4 mg/L alkalinity as  $HCO_3^-$ . The computed value is 204.1.

Note the slight bias forming in the results. Instead of exactly 203.4 mg/L, the value is 0.70 mg/L higher. This difference is due to non-ideal effects and the precise pH choice. The equations provided above are for ideal conditions. However, we are well aware that there are non-ideal effects that must be considered.

## Hydroxide

- ✓ Select the Alkalinity-Hydroxide brine analysis stream
- ✓ Remove the 100 mg/L HCO3-1 and add 100 mg/L OH<sup>-</sup>

Variable	Value	Balanced		
Cation	s (mg/L)			
Na+1	C	.0 135.177		
Anions (mg/L)				
OH-1	100.0	00 100.000		

✓ Select the Reconcile tab and recalculate

	Properties	Measured	Calculated
Т	emperature (°C)	25.0000	
P	ressure (atm)	1.00000	
p	н	0.0	11.7288
A	Ikalinity (mg HCO3/L)	0.0	361.285
D	ensity (g/ml)	0.0	0.997251
E	lec Cond, specific (µmho/cm)	0.0	1402.33
Т	otal Dissolved Solids (mg/L)	0.0	N/A
	Compo	sition Adjustments	
A	dd Charge Balance (mg/L Na+1)		135.177

The computed alkalinity is 361.3 mg/L as HCO<sub>3</sub><sup>-1</sup>. The formula weight of  $OH^-$  is 17.01 g/mole compared with 61.02 g/mole for  $HCO_3^{-1}$ , so 3.587 times more moles of  $OH^-$  is added compared with  $HCO_3^{-1}$ .

Therefore,

$$\frac{61020}{17010} \times 100 \frac{mg \text{ as } HCO_3^-}{L} = 358.7 \frac{mg \text{ as } HCO_3^-}{L}$$

Complete  $OH^-$  neutralization actually happens at about 10 pH, not 4.5 pH, which is the experimental endpoint. Observing the neutralization effect requires a titration curve.

#### Task 2: Non-Carbonate Alkalinity Contributions

We will see complications arising when other species contribute to alkalinity because they affect the direct use of the alkalinity value in the carbonate/scale tendency equation. Contributing species include borate, phosphate, formate, acetate, propanate, bisulfide, and any anion that will accept H<sup>+</sup> ion above 4.5 pH.

#### Acetate

- ✓ Select the Alkalinity-Acetate brine analysis stream
- ✓ Zero out any existing concentrations and add 100 mg/L acetate C2H3O2-1

Variable	Value	Balanced		
Cations (mg/L)				
Na+1	0.0	38.9364		
Anions (m	ng/L)			
C2H3O2-1	100.000	100.000		

✓ Select the **Reconcile** tab and recalculate

Properties	Measured	Calculated	
Temperature (°C)	25.0000		
Pressure (atm)	1.00000		
pH	0.0	7.98623	
Alkalinity (mg HCO3/L)	0.0	68.8928	
Density (g/ml)	0.0	0.997059	
Elec Cond, specific (µmho/cm)	0.0	148.603	
Total Dissolved Solids (mg/L)	0.0	N/A	
Composition Adjustments			
Add Charge Balance (mg/L Na+1)		38.9364	

The computed alkalinity is  $68.9 \frac{mg}{L} as HCO_3^-$ . The acetate formula weight is 59.05 g/mole, close to  $HCO_3^-$  (61.02 g/mole). So, if all the acetate contributes to alkalinity, then 100 mg/L acetate should be close to that for 100 mg/L  $HCO_3^-$  as shown in the following equation:

$$\frac{\frac{61020 \frac{mg HCO_3^-}{mol}}{\frac{mg Acetate^-}{mol}} \times 100 \frac{mg Acetate^-}{L} = 103.3 \frac{mg}{L} as HCO_3^-$$

The theoretical alkalinity contributed by acetate is  $103.3 \frac{mg}{l} as HCO_3^-$ . This means that  $\frac{68.95}{103.3} = 67\%$  of the acetate ion accepted an  $H^+$  at 4.5 pH (33% remained as the  $C_2H_3O_2^-$  ion). Acetate concentrations therefore have significant impact on total alkalinity.

#### Borate

- ✓ Select the Alkalinity-Borate brine analysis stream
- ✓ Remove any existing concentrations and add 100 mg/L borate, B(OH)4-1

Variable	Value	Balanced	
Cations (	Cations (mg/L)		
Na+1	0.0	29.1605	
Anions (r	Anions (mg/L)		
B(OH)4-1	100.000	100.000	

✓ Select the **Reconcile** tab and recalculate

Properties	Measured	Calculated	
Temperature (°C)	25.0000		
Pressure (atm)	1.00000		
рН	0.0	10.1258	
Alkalinity (mg HCO3/L)	0.0	79.5162	
Density (g/ml)	0.0	0.997103	
Elec Cond, specific (µmho/cm)	0.0	155.194	
Total Dissolved Solids (mg/L)	0.0	N/A	
Composition Adjustments			
Add Charge Balance (mg/L Na+1)		29.1605	

The borate contribution is 79.52  $\frac{mg}{L}$  as  $HCO_3^-$  for 100 mg/L added. If 100% borate contributed to alkalinity the maximum value would be:

$$\frac{61020 \frac{mg \ HCO_3^-}{mol}}{78835 \frac{mg \ B(OH)_4^-}{mol}} \times 100 \frac{mg \ B(OH)_4^-}{L} = 77.39 \frac{mg}{L} as \ HCO_3^-$$

The theoretical alkalinity is slightly lower than the computed amount (we will investigate this next). Thus, borate appears to be significant contributor to alkalinity. However, the pH is high, 10.12. Borate is generally neutralized to boric acid by ~7 pH. Consequently, only a fraction of the total boron in produced water is in anion form. Most is found in the acidic form  $H_3BO_3$ .

#### Sulfate

- ✓ Select the Alkalinity-Sulfate brine analysis stream
- ✓ Remove any existing concentrations and add 100 mg/L sulfate (S $O_4^{-2}$ )

Variable	Value	Balanced	
Cations (mg/L)			
Na+1	0.0	47.8641	
Anions (mg/L)			
SO4-2	100.000	100.000	

✓ Select the **Reconcile** tab and recalculate

Properties	Measured	Calculated	
Temperature (°C)	25.0000		
Pressure (atm)	1.00000		
pH	0.0	7.01280	
Alkalinity (mg HCO3/L)	0.0	2.20641	
Density (g/ml)	0.0	0.997122	
Elec Cond, specific (µmho/cm)	0.0	252.858	
Total Dissolved Solids (mg/L)	0.0	N/A	
Composition Adjustments			
Add Charge Balance (mg/L Na+1)		47.8641	

The sulfate contribution is 2.2 mg/L as  $HCO_3^-$  for 100 mg/L  $SO_4^{-2}$  added. If 100% sulfate contributed to alkalinity the maximum value would be:

$$\frac{\frac{61020 \frac{mg \ HCO_3^-}{mol}}{96060 \frac{mg \ SO_4^{-2}}{mol}} \times 100 \frac{mg \ SO_4^{-2}}{L} = 63.52 \frac{mg}{L} as \ HCO_3^{-2}$$

Sulfate has negligible effects on alkalinity. This is not surprising, since  $SO_4^{-2}$  is a salt of an acidic anion  $HSO_4^{-}$ . To reach the theoretical contribution of  $63.52 \frac{mg}{L} as HCO_3^{-}$ , the endpoint pH would be near 0.3.

#### Chloride

- ✓ Select the Alkalinity-Chloride brine analysis stream
- ✓ Remove any existing concentration and add 100 mg/L chloride (CI-)

Variable	Value	Balanced	
Cations (mg/L)			
Na+1	0.0	64.8463	
Anions (mg/L)			
CI-1	100.000	100.000	

✓ Select the **Reconcile** tab and recalculate

Properties	Measured	Calculated	
Temperature (°C)	25.0000		
Pressure (atm)	1.00000		
pH	0.0	6.99650	
Alkalinity (mg HCO3/L)	0.0	2.04107	
Density (g/ml)	0.0	0.997105	
Elec Cond, specific (µmho/cm)	0.0	342.904	
Total Dissolved Solids (mg/L)	0.0	N/A	
Composition Adjustments			
Add Charge Balance (mg/L Na+1)		64.8463	

The chloride contribution is 2.04 mg/L as bicarbonate for 100 mg/L Cl<sup>-</sup> added. If 100% chloride contributed to alkalinity the maximum value would be:

$$\frac{61020 \frac{mg HCO_3^-}{mol}}{35453 \frac{mg Cl^-}{mol}} \times 100 \frac{mg Cl^-}{L} = 172.1 \frac{mg}{L} as HCO_3^-$$

Chloride has negligible effects on alkalinity for the same reason as sulfate. Both are conjugate bases of strong acids. To reach the theoretical contribution of 172.1  $\frac{mg}{L}$  as  $HCO_3^-$ , the endpoint pH would be about 5.

#### Bisulfide

- ✓ Select the Alkalinity-Bisulfide brine analysis stream
- ✓ Remove any existing concentration and add 100 mg/L bisulfide (HS<sup>-</sup>)

	Variable	Value	Balanced	
Г	Cations (mg/L)			
	Na+1	0.0	69.5108	
	Anions (mg/L)			
	HS-1	100.000	100.000	

✓ Select the **Reconcile** tab and recalculate

Properties	Measured	Calculated	
Temperature (°C)	25.0000		
Pressure (atm)	1.00000		
pH	0.0	9.19343	
Alkalinity (mg HCO3/L)	0.0	186.132	
Density (g/ml)	0.0	0.997097	
Elec Cond, specific (µmho/cm)	0.0	337.862	
Total Dissolved Solids (mg/L)	0.0	N/A	
Composition Adjustments			
Add Charge Balance (mg/L Na+1)		69.5108	

The calculated bisulfide contribution is 186.13  $\frac{mg}{L}$  as  $HCO_3^-$  for 100 mg/L added. If 100% sulfate contributed to alkalinity the maximum value would be:

$$\frac{\frac{61020 \frac{mg HCO_{3}^{-}}{mol}}{33070 \frac{mg HS^{-}}{mol}} \times 100 \frac{mg HS^{-}}{L} = 184.5 \frac{mg}{L} as HCO_{3}^{-}$$

The theoretical bisulfide ion alkalinity is  $184.5 \frac{mg}{L} as HCO_3^-$ . It has a significant impact on alkalinity. Bisulfide concentrations however are generally low in produced water. Therefore, the absolute effects are small.

A summary of all the calculation results are shown in the table below.

100 mg/L of the following ion	Initial pH	Alkalinity as mg/L HCO3
HCO3-	8.27	100.66
CO3-2	10.64	204.1
OH-	11.73	361.29
Acetate-	7.99	68.89
B(OH)4-	10.13	79.52
SO4-2	7.01	2.21
CI-	6.99	2.04
HS-	9.19	186.13

#### Task 3: Alkalinity Titration Curves

The alkalinity endpoint provides a snapshot of fluid chemistry. A complete titration curve shows the system behavior across the pH profile and therefore the buffering region of different bases. In this section, we will create alkalinity titration curves for 100 mg/L of  $HCO_3^-$ ,  $CO_3^{-2}$ ,  $OH^-$ , Acetate<sup>-</sup>, and  $B(OH)_4^-$ .

The first two sections below are alternatives. Clients can either use **OLI Studio: ScaleChem** objects to create the 1N HCL reagent or use the **OLI Studio: Stream Analyzer** module.

#### Task 3-1 Create the 1N HCl Reagent with OLI Studio: ScaleChem

- ✓ Add a new brine analysis Add Brine Analysis
- ✓ Name it **1N HCI-1**
- ✓ Type HCL in the neutrals section with 36,453 mg/L
- ✓ Select the show non-zero box

	Variable	Value	Balanced
	Cations	s (mg/L)	
	Anions	s (mg/L)	
	Neutral	s (mg/L)	
HCI		36453.0	36453.0

✓ Select the **Reconcile** tab then calculate

Properties	Measured	Calculated
Temperature (°C)	25.0000	
Pressure (atm)	1.00000	
pH	0.0	0.0756504
Alkalinity (mg HCO3/L)	0.0	0.0
Density (g/ml)	0.0	1.01481
Elec Cond, specific (µmho/cm)	0.0	3.33828e5
Total Dissolved Solids (mg/L)	0.0	N/A

It should not be surprising that the reagent pH is almost zero. HCl is a strong acid, and thus the H-Cl bond is weak, resulting in near complete dissociation. Thus, there is 1 mole  $H^+$  in solution or zero pH.

✓ Save the file

#### Task 3-2 Create the 1N HCl Reagent with OLI Studio: Stream Analyzer

✓ Select the Global Streams icon in the Navigator pane



✓ Double-click the Add Stream icon in the Actions pane



- ✓ Press the <F2> key and change the name to 1N HCI-2
- ✓ Select the Units Manager icon then use the Quicklist button to pick Metric, concentration

			55 5092	Summary
Jnits Manager - 1N HC	I-2		? ×	Unit Set: Metric (moles)
Jnits Manager				Automatic Chemistry Model Aqueous (H+ ion) Databanks:
Metric	Batch ~	Moles	~	Quick List
				Metric, moles
				Metric, concentration
				Metric, molar concentration
Customize				Metric, mass fraction
Customizern				Metric, mole fraction
				SI, moles / ESP SI
				English, moles / ESP English
OK	Cancel	Apply	Help	Metric, flowing, moles / ESP Metric
	- 7.5			Metric, flowing, concentration
				Metric, flowing, molar concentration

✓ Press OK then enter HCI as an inflow with a concentration 36,453 mg/L

#### Task 3-3 Create an Alkalinity Titration

Once we complete either of the above methods for creating the HCl reagent stream, we can proceed with the following tasks.

- ✓ Add a Mixing Water object Y Add Mixing Water
- ✓ Rename it Alkalinity Titrator

First Sec

 Change the Brine Volumes to ml (per day) by clicking a blue-colored unit and opening the Units Manager

	Composition Parameters Corrosion Inlets	
	Variable	Units
	Brine Quantity	ml/day 🛛
	Oil Quantity	ml/day
	Gas Quantity	cm3/day
Туре	Whole Fluid Quantity	m3/day E3m3/day
Srine (m3/day)		E6m3/day
ond Brine (m3/day)		ft3/day 🗸

✓ Select the bottom right corner of the Name cell and pick 1N HCL-1 as the first brine

Note: Remember that first brine is the stream that the Mixer will adjust.

✓ Set the total volume to 1000 mL/day

[	Туре	Name	Flow
	First Brine (ml/day)	1N HCI-1	1000.00
	Second Brine (ml/day)	~	

The 1L volume is the total liquid volume (sum of 1<sup>st</sup> and 2<sup>nd</sup> brine). In this case, the 1L will be primarily the alkalinity liquid that we will enter next. The 1N HCl reagent will be added to the Alkalinity liquid, but its volume will be relatively small. It is an imperfect example, but it serves to show another application of the *Mixing tool*. The actual flow rate is unimportant, but for realism, we will use a volume similar to laboratory conditions.

#### Task 3-4 Bicarbonate Titration Curve

✓ Select the bottom right corner of the Name cell in the Second Brine row and pick the *Alkalinity-Bicarbonate* (the original Alkalinity brine) as the second brine

Γ	Туре	Name	Flow
Γ	First Brine (ml/day)	1N HCI-1	1000.00
	Second Brine (ml/day)	Alkalinity-Bicarbonate	

- ✓ Go to the Conditions tab
- ✓ Change the type from **Ratio** to **Flow**

Select Type	e		Brine Flows	
	014/		1N HCI-1 (ml/day)	Alkalinity-Bicarbonate
	000	·	1000.00	0.0
Total flow	: 1000.0	00 ml/dav	800.000	200.000
		,	600.000	400.000
Channel	5		400.000	600.000
Steps:	<u> </u>	Auto Step	200.000	800.000
			0.0	1000.00
			5	

✓ Type 2 in the first column and first row then press tab and type 0 in the second row

Brine Flows	
1N HCI-1 (ml/day)	Alkalinity-Bicarbonate
2.00000	998.000
0.0	1000.00
600.000	400.000
400.000	600.000
200.000	800.000
0.0	1000.00

✓ Change the Auto Steps amount to 20 then select the Auto Step button



The software will add the HCl at 0.1 mL increments up to 2 mL. It will also remove 0.1 mL of *Alkalinity-HCO3* volume at each step to maintain the 1000 mL volume. Consequently, the titration we are doing is not 100% correct. In an actual titration, the sample fluid volume is fixed at 100 mL. Fortunately, the HCl reagent is concentrated, and the volume added is small. This limits the displacement error to 0.2%

Select Type	Brine Flows	
Elow	1N HCI-1 (ml/day)	Alkalinity-Bicarbonate
Flow	2.00000	998.000
Total flow: 1000.00 ml/day	1.90000	998.100
. ,	1.80000	998.200
Stops: 20 Auto Stop	1.70000	998.300
Auto Step	1.60000	998.400
	1.50000	998.500
	1.40000	998.600
	1.30000	998.700
	1.20000	998.800
	1.10000	998.900
	1.00000	999.000
	0.900000	999.100
	0.800000	999.200
	0.700000	999.300
	0.600000	999.400
	0.500000	999.500
	0.400000	999.600
	0.300000	999.700
	0.200000	999.800
	0.100000	999.900
	0.0	1000.00

- ✓ Press the Calculate button
- ✓ Select the Plot tab and then select the Variables button
- Remove all existing plot variables in the Y1 Axis by highlight the Y1 axis header then select the << arrow button</li>



- ✓ Expand the Aqueous category and add HCO3-1 to the Y1 axis
- ✓ Expand the Additional Stream Parameters category and add pH-Aqueous to the Y2 axis



✓ Press **OK** and view the plot



The pH curve is the typical bicarbonate-buffering curve. The slope of the curve is shallow between pH 7 and 5.5, where bicarbonate buffering is strong. Below 5.5 pH, the curve drops sharply and has its steepest slope at about 4.5 pH.

✓ Click the View Data button

	1N HCI-1 Flow	HCO3-1	рН
	ml/day	mg/L	
1	2.00000	0.136221	3.45629
2	1.90000	0.186411	3.59319
3	1.80000	0.294252	3.79238
4	1.70000	0.662394	4.14685
5	1.60000	3.15476	4.83606
6	1.50000	8.64414	5.29927
7	1.40000	14.5983	5.55620
8	1.30000	20.6342	5.73841
9	1.20000	26.6969	5.88490
10	1.10000	32.7715	6.01163
11	1.00000	38.8520	6.12687
12	0.900000	44.9357	6.23574
13	0.800000	51.0208	6.34199
14	0.700000	57.1061	6.44885
15	0.600000	63.1903	6.55967
16	0.500000	69.2717	6.67862
17	0.400000	75.3472	6.81177
18	0.300000	81.4104	6.96974
19	0.200000	87.4421	7.17511
20	0.100000	93.3526	7.49486
21	0.0	97.6983	8.26888

- ✓ Copy the data to a spreadsheet program by holding down the left arrow, highlighting all the points and pressing <Ctrl+C>.
- ✓ Click on the View Plot button to show the plot again

🛛 🖸	View Plot	Variables	Options
-----	-----------	-----------	---------

For the following titrations, we can either add a new Mixing Water object or work from the existing object. The instructions below assume the latter.

#### Task 3-5 Carbonate Titration Curve

- ✓ Return to the **Design** | **Inlets** screen
- ✓ Replace the second brine with the *Alkalinity Carbonate* stream

🖌 Alkal 🧭 Des	inity Titrator cription 🔮 Design 🚮	Plot 👼 Report	
ets	Туре	Name	Flow
Inlets	Type First Brine (ml/day)	Name 1N HCI-1	Flow 1000.00
Inlets	First Brine (ml/day) Second Brine (ml/day)	Name 1N HCI-1 Alkalinity-Carbonate	Flow 1000.00

✓ Select the **Conditions** tab and change the 1N HCl flow from 2 ml to 4 ml (top cell)

Brine Flows	
1N HCI-1 (ml/day)	Alkalinity-Carbona
4	998.000
1.90000	998.100

We will need twice as much acid to titrate the  $CO_3^{-2}$ 

✓ Make sure Auto steps are set at 20 and click on the Auto Step button then click on the calculate button



- ✓ Select the **Plot** tab then select the **Variables** button
- ✓ Add CO3-2 from the Aqueous categories to the Y1 Axis



✓ Press OK and view the Plot



- ✓ Click on the View Data button then copy data to a spreadsheet program
- ✓ Click on the View Plot button to show the plot again
- ✓ Save the file

#### Task 3-6 Hydroxide Titration Curve

✓ Return to the **Design** | **Inlets** tabs and replace the Carbonate stream with Hydroxide

Alkalin	ity Tit	rator			
🎻 Descri	iption	🕺 Design	🛍 Ple	ot <u> </u> Report	
ets	]	Туре		Name	Flow
Inlets	First Br	Type rine (ml/day)	11	Name	Flow 1000.00

- ✓ Select the **Conditions**, tab then overwrite the first cell with 7 ml
- ✓ Press the Auto Step button and then click the calculate button

¥	Y Alkalinity Titrator													
4	🕈 Des	scription 🔮 Design 🛍 Plot												
	ets	Select Type	Brine Flows			Calculate 🥥								
	Inline	Flow Total flow: 1000.00 ml/day	1N HCI-1 (ml/day)	Alkalinity-Hydroxi										
			7.00000	993.000										
			6.65000	993.350		Summary								
		Steps: 20 Auto Step	6.30000	993.700		Unit Cate a Constant								
			5.95000	994.050		Unit Set: <custom></custom>								

- ✓ Select the **Plot** tab then select the **Variables** button
- ✓ Remove the carbonates by double clicking on them
- ✓ Add OH- from the Aqueous section to the Y1 axis, and add pH in the Y2 axis



- ✓ Select the View Data button and copy the data to a spreadsheet
- ✓ Click on the **View Plot** button to show the plot again
- ✓ Save the file

#### Task 3-7 Acetate Titration Curve

✓ Repeat the same procedure for Acetate

¥ Alkal	inity Tit				
🛷 Des	cription	🥸 Design 🏾	📶 Plot	😼 Report	
		J.			
ets		Туре		Name	Flow
Inlets	First B	Type rine (ml/day)	1N H	Name CI-1	Flow 1000.00

- ✓ Select the **Conditions**, tab then overwrite the first cell with 2 ml
- ✓ Reset the Auto Steps to 20
- ✓ Press calculate then plot pH on the Y2 Axis and acetate ion (C2H3O2-1)to the Y1 axis



- ✓ Save the file
- ✓ Click on the View Data button then copy the data to a spreadsheet program
## Task 3-8 Borate Titration Curve

- ✓ Redo the calculation for Borates
- ✓ Decide upon which species are important to plot



- ✓ Click on the View Data button and copy data to a spreadsheet program
- ✓ Save the file

## Task 3-9 Sulfate Titration Curve

✓ Repeat for Sulfate



The sulfate titration calculation was taken well beyond the alkalinity endpoint in order to show the equilibrium between the  $SO_4^{-2}$  and  $HSO_4^{-2}$  species. At ~2 pH,  $SO_4^{-2}$  and  $HSO_4^{-2}$  have roughly the same concentration: this is a sulfate buffering region.

- ✓ Click on the **View Data** button and copy the data to a spreadsheet program
- ✓ Save the file

#### Task 3-10 Interpreting the Titration Data

- ✓ Move to the spreadsheet
- ✓ Plot the pH vs. HCl



This plot shows the buffering (pH) regions and the total buffering capacity of each weak acid. The highest buffering capacity, though not relevant to produced waters, is OH<sup>-</sup>. It's relatively low molecular weight (17 g/mol) results in more buffering per concentration (all are fixed at 100 mg/l). Its buffering region ends at about 10.5 pH (extent of shallow slope). At this pH virtually all the OH is consumed by the HCl titrant. Consequently, at typical produced water pH (between 5 and 8) no OH<sup>-</sup> buffering occurs.

✓ Plot the species concentrations vs. pH



The plot above shows the concentration impact in greater detail. It represents the concentration of free ion vs. pH for the different buffers. The red vertical line to the far left is the pH titration end point. The shaded vertical section to the right is the typical produced water pH as measured in the laboratory. From this diagram we can see that very little OH<sup>-</sup> exists in produced water between 7 and 8 pH.

The carbonate ion is dibasic (accepts two H<sup>+</sup>) and therefore has two buffering regions and endpoints. The first buffering zone exists from 10.7 to 9 pH, and the sharp pH drop reflects  $CO_3^{-2}$  depletion from solution. Few produced waters have pH above 8, and therefore  $CO_3^{-2}$  alkalinity is rarely observed. The second buffering region of  $CO_3^{-2}$  is associated with protonating  $HCO_3^{-}$ , and this second zone parallels exactly the 100 m/l  $HCO_3^{-1}$  titration curve. This second curve is the main alkalinity component in produced waters. Its existence is due to the continuous production of  $CaCO_{3(s)}$  in seawater.

The acetate buffering zone is between about 5.7 and 3.5 (end of curve). If the titration were extended, then the inflection point ~2.7 pH would have been observed. This buffering zone straddles the alkalinity endpoint, which is why it creates complications when measuring total alkalinity without an organic acid content. Organic acids are products of organics/kerogen catagenesis, which creates the fossil fuel. Therefore, it is commonly observed in produced waters. Lastly, the borates buffering region is between 10 and 8 pH with an end point at about 6 pH. Borates exist at pH's higher than the

typical produced water, but when borate concentrations are high and the laboratory measured pH approaches or exceeds 8, then this base will affect total alkalinity. Borates exist in seawater and deposit in the interstices of sediments. They are also fairly soluble (like CI and Na) and are generally found in produced waters.

The table below contains the pH and concentration data from the calculations we ran and plotted above. The shaded cells represent the regions in the titration curves that would contribute to a produced water alkalinity. At the bottom of the table is a % range value. This value represents the fraction of the species concentration that would contribute to the alkalinity.

HCO3-	1	СО	3-2	0	H-	Ace	tate-1	BOł	-14-1	SC	)4-2	н	IS-
pН	mg/l	рΗ	mg/l	рΗ	mg/l	рΗ	mg/l	рΗ	mg/l	рΗ	mg/l	рΗ	mg/l
3.5	0	3.2	0	2.8	0	3.4	4	3.2	0	2.8	87	3.0	0
3.6	0	3.3	0	2.9	0	3.5	6	3.2	0	2.8	88	3.1	0
3.8	0	3.6	0	3.1	0	3.7	7	3.3	0	2.8	88	3.3	0
4.1	1	4.1	0	3.3	0	3.8	10	3.4	0	2.8	89	3.4	0
4.8	3	5.2	0	3.8	0	3.9	13	3.5	0	2.9	89	3.8	0
5.3	9	5.7	0	10.3	4	4.1	17	3.7	0	2.9	90	4.9	1
5.6	15	6.0	0	10.7	10	4.2	21	3.9	0	2.9	90	5.9	7
5.7	21	6.2	0	11.0	17	4.3	26	4.5	0	2.9	91	6.2	14
5.9	27	6.4	0	11.1	23	4.4	31	8.0	5	3.0	91	6.4	20
6.0	33	6.6	0	11.2	29	4.5	37	8.4	13	3.0	92	6.5	27
6.1	39	6.9	0	11.3	36	4.6	42	8.6	21	3.1	92	6.7	34
6.2	45	7.4	0	11.4	42	4.7	48	8.8	28	3.1	93	6.8	40
6.3	51	8.8	4	11.4	49	4.8	54	9.0	36	3.2	94	6.9	47
6.4	57	9.5	14	11.5	55	4.9	59	9.1	44	3.2	94	7.0	54
6.6	63	9.7	24	11.5	62	5.0	65	9.2	51	3.3	95	7.1	60
6.7	69	10.0	34	11.6	68	5.2	71	9.4	58	3.4	95	7.3	67
6.8	75	10.1	43	11.6	74	5.3	77	9.5	66	3.5	96	7.4	73
7.0	81	10.3	51	11.6	81	5.4	82	9.6	73	3.6	97	7.6	80
7.2	87	10.4	59	11.7	87	5.6	88	9.8	79	3.8	97	7.8	87
7.5	93	10.5	66	11.7	94	6.0	94	10.0	84	4.1	98	8.1	93
8.3	98	10.6	71	11.7	100	8.0	100	10.1	89	7.0	99	9.2	99
% in range	93		0		0		63		5		1		79

Consider the following with this table: Anions are now being measured using ion chromatography. How does the alkalinity value measured relate to this ion chromatography measured ions?

#### Task 4: Effects of Temperature and Salinity on Carbonate Alkalinity

- ✓ Return to the original *Alkalinity* (or *Alkalinity-Bicarbonate*) brine
- ✓ Copy and paste it to create a new one
- ✓ Rename it Alkalinity-Bicarbonate-NaCl
- ✓ Add 23000 mg/l Na<sup>+</sup> and 35453 mg/l Cl<sup>-</sup>

🐱 Alka < Des	inity-Bicarbonate-NaCl cription 🐼 Design 🙀			
itry	Variable	Value	Balanced	Entry Options
ta En	Na+1	23000.0	23027.6	Units ma/L ~
Dai	Apione /			Display
	HC03-1	100.000	100.000	Formula 🗸
lcile	CI-1	35453.0	35453.0	Show Non-zero Only

- ✓ Return to the *Alkalinity Titrator* object and select the Inlets tab
- ✓ Change the second brine to the new *Alkalinity-Bicarbonate-NaCl* brine
- ✓ Set the Max HCl to 2ml and press the Auto Steps
- ✓ Calculate, Select the Plot tab, then the Variables button
- ✓ Remove all the variables from the Y1 and Y2 axes
- ✓ Add HCO<sub>3</sub><sup>-</sup> from the Aqueous category to the Y1 Axis and pH from the Additional Stream Parameters section in the Y2 Axis



- ✓ Copy the data to the Spreadsheet and add this plot with the original **HCO**<sub>3</sub><sup>-</sup> titration plot
- ✓ Click on the *Alkalinity Titration's* Inlets tab and change the temperature to **75C**
- ✓ Calculate

✓ Plot the pH vs. HCl for the three 100 mg/l HCO<sub>3</sub><sup>-</sup> calculations (25C, 25C & 1N NaCl, and 75C & 1N NaCl).



Consider the following when viewing the plot: Under ideal conditions (25C & 0 M NaCl) the titration endpoint occurs at ~1.65 ml HCl. At more realistic conditions (1m NaCl) the endpoint occurs at ~1.6 ml HCl. This is a difference of ~3%.

## Task 5: Effects of Temperature and Salinity on Acetate Alkalinity

- ✓ Return to the *Alkalinity-Bicarbonate-NaCl* brine
- ✓ Keep the 23000 mg/I Na<sup>+</sup> and 35453 mg/I Cl<sup>-</sup>
- $\checkmark$  Erase the HCO3-1 value and add 100 mg/l acetate<sup>-1</sup>, and then **Calculate**
- ✓ Return to the *Alkalinity Titrator* and set the maximum HCl to 2 ml
- ✓ Click on Auto Step
- ✓ Recalculate to create the following pH vs. HCl plot



Consider the following when viewing the plot: Under ideal conditions (25C & 0 M NaCl) the titration endpoint occurs at ~1.1 ml HCl. At more realistic conditions (1m NaCl) the endpoint occurs at 0.75 ml HCl. A difference of ~32%!

# Summary

The purpose of this chapter was to present the quantitative chemistry of alkalinity and to expose some additional calculation features within ScaleChem. From this, we can see that additional measurements for organic acids, bisulfides, and borates can be important when considering carbonate scale risks.

## Further Reading

SPE 37277 – Alkalinity in Oilfield Waters. What alkalinity is and how it is measured. 1996. B. Kaasa and T Ostvold. 1997 SPE international symposium on Oilfield Chemistry. Houston TX.

James Drever. 1988. The Geochemistry of Natural Waters, Chapter 4: The Carbonate System and pH control. Prentice Hall.

# Chapter 12 – Calculating Alkalinity

## **Overview**

In this chapter you will learn:

- How to calculate acid:anion ratios at varying ionic strengths
- Use the Mixing Water calculation as a pH titration apparatus
- Understand how weak acid chemistry affects alkalinity
- Compare true bicarbonate and carbonate concentrations to carbonate alkalinity

# Investigating the Components that Create Alkalinity

The alkalinity measurement is used to compute carbonate scale tendencies and pH buffer capacity. Bicarbonate, and to a lesser degree, borates, organic acids and bisulfides, provide alkalinity to produced water. Therefore, this chapter is an introduction to quantifying alkalinity beyond the standard contributions from  $HCO_3^-$ ,  $CO_3^{-2}$  and  $OH^-$ .

#### Carbonate Alkalinity Contributions

The Standard Methods for the Examination of Water and Wastewater codified the measurements to determine alkalinity. In its second edition (1912), the book linked alkalinity and total hardness to CaCO<sub>3</sub> scale (an interesting side note, in the year of publication, olive oil-derived castile soap was used to measure total water hardness instead of inductively coupled plasma spectrometry). Measurements related to Lacmoid, Erythrosine, Methyl orange, silver nitrate and phenolphthalein, were all designed to measure carbonate and hydroxide alkalinity. The contribution of non-carbonate and non-hydroxide buffers, like organic acids, do not have supporting text. Oilfield water analyses continue to use the original experimental design with the same endpoint, despite the measurement does not capture the produced water species complexity.

Alkalinity equations are a series of chemical reactions with measurable endpoints, described below:

 $\begin{aligned} HCO_3^{-2} + H^+ &= CO_2 + H_2O \ \ considerd \ complete \ by \ pH < 4.5 \ (25^\circ C) \\ CO_3^{-2} + H^+ &= HCO_3^- \ \ considerd \ complete \ by \ pH < 8.5 \ (25^\circ C) \\ OH^- + H^+ &= H_2O \ \ considerd \ \ complete \ by \ pH < 10 \ (25^\circ C) \end{aligned}$ 

Thus, a simple definition for carbonate alkalinity is:

Carbonate Alkalinity = Total  $H^+$  required to convert all  $CO_3^{-2}$ ,  $HCO_3^-$ , and  $OH^-$  to  $CO_2$ =  $H^+$  (from  $CO_3^{-2}$ ) +  $H^+$  (from  $HCO_3^-$  and neutralized  $CO_3^{-2}$ ) +  $H^+$  (from  $OH^-$ ) = total acid added to bring the pH to < 4.5

$$= 2CO_3^{-2} + HCO_3^{-} + OH^{-1}$$

Lastly, a mass balance equation for carbonate:

$$Carbonate_{Total} = HCO_3^- + CO_3^{-2}$$

A Bjerrum plot, in which carbonate concentration is fixed, shows the relative concentration of each species as functions of pH (also shown is the relative OH<sup>-</sup> concentration):



pH - Aqueous [pH]

The calculations provide measurable hydroxide, carbonate and bicarbonate concentrations at a relative pH: free hydroxide (OH-) exists above 10 pH; carbonate exists above 8.5 pH; and bicarbonate exists between 4.5 and 8.5 pH.

An alkalinity titration procedure is as follows:

- 1. Start with a known sample volume
- 2. Add two indicators the first activates at 8.5 pH or higher and the second is active below 4.5 pH
- 3. Titrate the sample with a strong acid of known composition

When the first indicator deactivates (the pH drops below 8.5), the amount of titrant added is the carbonate alkalinity and hydroxide alkalinity point. The following equation converts the acid volume to the carbonate alkalinity.

$$CO_{3}^{-} Alk\left(\frac{mg}{L}\right) as HCO_{3}^{-}$$

$$= Acid volume used to 8.5 pH(L) \times Acid Conc.\left(\frac{moles}{L}\right) \times 61020 \left(\frac{mg HCO_{3}^{-}}{mole}\right)$$

$$\times \frac{1}{Sample Vol(L)}$$

4. The sample is titrated further until it until the second indicator appears (pH<4.5). This is the bicarbonate alkalinity endpoint. This information is used as follows:

$$\begin{aligned} HCO_{3}^{-} Alk\left(\frac{mg}{L}\right) & as \ HCO_{3}^{-} \\ &= Vol \ Acid \ for \ Bicarbonate \ Alk \ Titration \ (L) \times Acid \ Conc. \left(\frac{moles}{L}\right) \\ &\times 61020 \ \left(\frac{mg \ HCO_{3}^{-}}{mole}\right) \times \frac{1}{Sample \ Vol \ (L)} \end{aligned}$$

The two titrations combine to calculate the total alkalinity

$$\begin{aligned} \text{Total Alk} & \left(\frac{mg}{L}\right) \text{ as } HCO_3^- \\ &= \text{Vol Acid for Carbonate Alk Titration (L)} \\ &+ \text{Vol Acid for Biarbonate Alk Titration (L)} \times \text{Acid Conc.} \left(\frac{\text{moles}}{L}\right) \\ &\times 61020 \left(\frac{mg \ HCO_3^-}{\text{mole}}\right) \times \frac{1}{\text{Sample Vol (L)}} \end{aligned}$$

$$OH^{-}Alk\left(\frac{mg}{L}\right) as HCO_{3}^{-} = CO_{3}^{-}Alk\left(\frac{mg}{L}\right) - HCO_{3}^{-}Alk\left(\frac{mg}{L}\right)$$

 In the absence of carbonates or in addition to carbonate, the OH<sup>-</sup> alkalinity can also be determined from the difference between the carbonate and bicarbonate alkalinity and is only relevant above 9.5 or 10pH (OH<sup>-</sup>>10<sup>-4.5</sup> M or ~0.5ppm).

$$Alk_{OH} = 2 * Alk_{8.5pH EP} - Alk_{4.5pH EP}$$

If the value is negative, then there is no hydroxide alkalinity. Hydroxide alkalinity is not common in production waters because the pH is never that high. It is present in drilling and alkaline injection fluids.

#### **Problem Statement**

Oilfield waters do not conform chemically, to the fresh water used in the original alkalinity method. Organic acids, borates, phosphates, sulfides and other proton-accepting species produce alkalinity. Consequently, the standard alkalinity titration cannot be used to measure the bicarbonate/carbonate concentration. We will evaluate this in the following examples.

#### Task 1: Quantifying Alkalinity of Certain Anions

You will compute the alkalinity of 100 mg/L of the following anions:  $HCO_3^-$ ,  $CO_3^{-2}$ ,  $OH^-$ ,  $CH_3CO_2^-$ ,  $B(OH)_4^-$ ,  $SO_4^{-2}$ ,  $CI^-$  and HS. The counter-ion will be sodium making the system basic. There will be no additional salt (salinity) added the first set of calculations. This will allow you to quantify alkalinity at near-ideal activities. You will calculate a second time in the presence of 1M NaCl. You will conclude this section by producing a quantitative table showing the contribution to alkalinity as a function of species and salinity.

We will be using °C and atm units for Temperature and Pressure so please adjust accordingly.

- ✓ Create a new file called "Alkalinity"
- ✓ Add a new brine analysis
- ✓ Rename it *Alkalinity*

SSC B	SSC Basics - Chapter 20 - Alkal					
🍓 Str	eams					
<b>)</b>	Alkalinity					

#### Bicarbonate

- ✓ Select the **Design** tab
- ✓ Find HCO3-1 in the Anions grid and give it a value of 100 mg/L
- ✓ Check the **Non-zero only** box

Variable	Value	Balanced	Entry Options
Cations (n	ng/L)		Units
Na+1	0.0	37.6778	mg/L ~
			Display
Anions (n	E-maile and		
HCO3-1	100.000	100.000	Formula
			Show Non-zero Only

- ✓ Select the **Reconcile** tab
- ✓ Leave the default reconciliation option (Concentration Data Only)
- ✓ Click **calculate** and document the pH and alkalinity

Properties	Measured	Calculated
Temperature (°C)	25.0000	
Pressure (atm)	1.00000	
рН	0.0	8.26888
Alkalinity (mg HCO3/L)	0.0	100.660
Density (g/ml)	0.0	0.997086
Elec Cond, specific (µmho/cm)	0.0	150.960
Total Dissolved Solids (mg/L)	0.0	N/A
Compo	sition Adjustments	
Add Charge Balance (mg/L Na+1)		37.6778

The calculated pH is 8.27. The calculated alkalinity is 100.7 mg/L and is entirely the bicarbonate alkalinity. The 0.7 mg/L addition to the alkalinity value is due to the pH endpoint and minor activity coefficient effects.

The next three steps will make it easier for us to perform titrations later. Alternatively, we can continue working in the same *Alkalinity* file and replace the anions as we go along. Subsequent instructions will be applicable for both approaches.

✓ In the Navigator pane, right-mouse click *Alkalinity* and press copy



Right-mouse click the Streams icon, then select paste. Repeat this 7 times, to create a total of 8 objects in the navigator panel.

♦ Stree		Descri
	Arrange	>
	Cut	
	Сору	
	Paste	

The software designates the new streams as Alkalinity -1, Alkalinity-2, and so on.

✓ Rename the objects so that the anion they contain will be easily identifiable: Alkalinity-Bicarbonate, Alkalinity-Carbonate, Alkalinity-Hydroxide, Alkalinity-Acetate, Alkalinity-Borate, Alkalinity-Sulfate, Alkalinity-Chloride, and Alkalinity-Bisulfide



## Carbonate

- ✓ Select the Alkalinity-Carbonate brine analysis stream
- ✓ Remove the 100 mg/L HCO3-1 and add 100 mg/L CO3-2
- ✓ Check the Non-zero only box

Cations	(mg/L)		
Ma+1			Units
2 ·····	0.0	76.6214	mg/L 🗸
Da			Display
Anions	mg/L)		Earmula V
C03-2	100.000	100.000	
g			Show Non-zero Only
Neutrals	(mg/L)		Show Balanced Column
U U			

• You can either type in CO3-2 in an empty cell, or select the **Expanded Template** to locate it in the Anion grid.

✓ Select the **Reconcile** tab and recalculate

Properties	Measured	Calculated
Temperature (°C)	25.0000	
Pressure (atm)	1.00000	
рН	0.0	10.6347
Alkalinity (mg HCO3/L)	0.0	204.114
Density (g/ml)	0.0	0.997171
Elec Cond, specific (µmho/cm)	0.0	431.288
Total Dissolved Solids (mg/L)	0.0	N/A
Compo	sition Adjustments	
Add Charge Balance (mg/L Na+1)		76.6214

The alkalinity is 204.1 mg/L as  $HCO_3^-$  twice the  $CO_3^{-2}$  concentration added, and is consistent with the above equation. The  $HCO_3^-$  formula weight is 61.02 g/mole and  $CO_3^{-2}$  is 60.01 g/mole – a mole ratio of 1.7%. Two factors contribute to the alkalinity increase. The first is that  $CO_3^{-2}$  accepts two  $H^+$  ions one above 8.5 pH and one above 4.5 pH. The second is that 1.7% additional moles of carbonate are added because of the weight difference. Thus, the theoretical alkalinity of 100 mg/L alkalinity as  $HCO_3^-$  \*2 \* 1.7% = 203.4 mg/L alkalinity as  $HCO_3^-$ . The computed value is 204.1.

Note the slight bias forming in the results. Instead of exactly 203.4 mg/L, the value is 0.70 mg/L higher. This difference is due to non-ideal effects and the precise pH choice. The equations provided above are for ideal conditions. However, we are well aware that there are non-ideal effects that must be considered.

## Hydroxide

- ✓ Select the Alkalinity-Hydroxide brine analysis stream
- ✓ Remove the 100 mg/L HCO3-1 and add 100 mg/L OH<sup>-</sup>

Variable	Value	Balanced				
Cations (mg/L)						
Na+1	C	.0 135.177				
Anions (mg/L)						
OH-1	100.0	00 100.000				

✓ Select the Reconcile tab and recalculate

	Properties	Measured	Calculated
Т	emperature (°C)	25.0000	
P	ressure (atm)	1.00000	
p	н	0.0	11.7288
A	Ikalinity (mg HCO3/L)	0.0	361.285
D	ensity (g/ml)	0.0	0.997251
E	lec Cond, specific (µmho/cm)	0.0	1402.33
Т	otal Dissolved Solids (mg/L)	0.0	N/A
	Compo	sition Adjustments	
A	dd Charge Balance (mg/L Na+1)		135.177

The computed alkalinity is 361.3 mg/L as HCO<sub>3</sub><sup>-1</sup>. The formula weight of  $OH^-$  is 17.01 g/mole compared with 61.02 g/mole for  $HCO_3^{-1}$ , so 3.587 times more moles of  $OH^-$  is added compared with  $HCO_3^{-1}$ .

Therefore,

$$\frac{61020}{17010} \times 100 \frac{mg \text{ as } HCO_3^-}{L} = 358.7 \frac{mg \text{ as } HCO_3^-}{L}$$

Complete  $OH^-$  neutralization actually happens at about 10 pH, not 4.5 pH, which is the experimental endpoint. Observing the neutralization effect requires a titration curve.

#### Task 2: Non-Carbonate Alkalinity Contributions

We will see complications arising when other species contribute to alkalinity because they affect the direct use of the alkalinity value in the carbonate/scale tendency equation. Contributing species include borate, phosphate, formate, acetate, propanate, bisulfide, and any anion that will accept H<sup>+</sup> ion above 4.5 pH.

### Acetate

- ✓ Select the Alkalinity-Acetate brine analysis stream
- ✓ Zero out any existing concentrations and add 100 mg/L acetate C2H3O2-1

Variable	Value	Balanced				
Cations (mg/L)						
Na+1	0.0	38.9364				
Anions (mg/L)						
C2H3O2-1	100.000	100.000				

✓ Select the **Reconcile** tab and recalculate

Properties	Measured	Calculated
Temperature (°C)	25.0000	
Pressure (atm)	1.00000	
pH	0.0	7.98623
Alkalinity (mg HCO3/L)	0.0	68.8928
Density (g/ml)	0.0	0.997059
Elec Cond, specific (µmho/cm)	0.0	148.603
Total Dissolved Solids (mg/L)	0.0	N/A
Comp	osition Adjustments	
Add Charge Balance (mg/L Na+1)		38.9364

The computed alkalinity is  $68.9 \frac{mg}{L} as HCO_3^-$ . The acetate formula weight is 59.05 g/mole, close to  $HCO_3^-$  (61.02 g/mole). So, if all the acetate contributes to alkalinity, then 100 mg/L acetate should be close to that for 100 mg/L  $HCO_3^-$  as shown in the following equation:

$$\frac{61020 \frac{mg HCO_3^-}{mol}}{59050 \frac{mg Acetate^-}{mol}} \times 100 \frac{mg Acetate^-}{L} = 103.3 \frac{mg}{L} as HCO_3^-$$

The theoretical alkalinity contributed by acetate is  $103.3 \frac{mg}{l} as HCO_3^-$ . This means that  $\frac{68.95}{103.3} = 67\%$  of the acetate ion accepted an  $H^+$  at 4.5 pH (33% remained as the  $C_2H_3O_2^-$  ion). Acetate concentrations therefore have significant impact on total alkalinity.

#### Borate

- ✓ Select the Alkalinity-Borate brine analysis stream
- ✓ Remove any existing concentrations and add 100 mg/L borate, B(OH)4-1

Variable	Value	Balanced	
Cations (	Cations (mg/L)		
Na+1	0.0	29.1605	
Anions (r	Anions (mg/L)		
B(OH)4-1	100.000	100.000	

✓ Select the **Reconcile** tab and recalculate

Properties	Measured	Calculated		
Temperature (°C)	25.0000			
Pressure (atm)	1.00000			
рН	0.0	10.1258		
Alkalinity (mg HCO3/L)	0.0	79.5162		
Density (g/ml)	0.0	0.997103		
Elec Cond, specific (µmho/cm)	0.0	155.194		
Total Dissolved Solids (mg/L)	0.0	N/A		
Composition Adjustments				
Add Charge Balance (mg/L Na+1)		29.1605		

The borate contribution is 79.52  $\frac{mg}{L}$  as  $HCO_3^-$  for 100 mg/L added. If 100% borate contributed to alkalinity the maximum value would be:

$$\frac{61020 \frac{mg \ HCO_3^-}{mol}}{78835 \frac{mg \ B(OH)_4^-}{mol}} \times 100 \frac{mg \ B(OH)_4^-}{L} = 77.39 \frac{mg}{L} as \ HCO_3^-$$

The theoretical alkalinity is slightly lower than the computed amount (we will investigate this next). Thus, borate appears to be significant contributor to alkalinity. However, the pH is high, 10.12. Borate is generally neutralized to boric acid by ~7 pH. Consequently, only a fraction of the total boron in produced water is in anion form. Most is found in the acidic form  $H_3BO_3$ .

#### Sulfate

- ✓ Select the Alkalinity-Sulfate brine analysis stream
- ✓ Remove any existing concentrations and add 100 mg/L sulfate (S $O_4^{-2}$ )

Variable	Value	Balanced	
Cations (mg/L)			
Na+1	0.0	47.8641	
Anions (mg/L)			
SO4-2	100.000	100.000	

✓ Select the **Reconcile** tab and recalculate

	Properties	Measured	Calculated		
Temperatu	ire (°C)	25.0000			
Pressure (	atm)	1.00000			
pH		0.0	7.01280		
Alkalinity (	ng HCO3/L)	0.0	2.20641		
Density (g/	íml)	0.0	0.997122		
Elec Cond	, specific (µmho/cm)	0.0	252.858		
Total Diss	olved Solids (mg/L)	0.0	N/A		
	Composition Adjustments				
Add Charg	e Balance (mg/L Na+1)		47.8641		

The sulfate contribution is 2.2 mg/L as  $HCO_3^-$  for 100 mg/L  $SO_4^{-2}$  added. If 100% sulfate contributed to alkalinity the maximum value would be:

$$\frac{\frac{61020 \frac{mg \ HCO_3^-}{mol}}{96060 \frac{mg \ SO_4^{-2}}{mol}} \times 100 \frac{mg \ SO_4^{-2}}{L} = 63.52 \frac{mg}{L} as \ HCO_3^{-2}$$

Sulfate has negligible effects on alkalinity. This is not surprising, since  $SO_4^{-2}$  is a salt of an acidic anion  $HSO_4^{-}$ . To reach the theoretical contribution of  $63.52 \frac{mg}{L} as HCO_3^{-}$ , the endpoint pH would be near 0.3.

#### Chloride

- ✓ Select the Alkalinity-Chloride brine analysis stream
- ✓ Remove any existing concentration and add 100 mg/L chloride (CI-)

Variable	Value	Balanced
Cations (mg/L)		
Na+1	0.0	64.8463
Anions (mg/L)		
CI-1	100.000	100.000

✓ Select the **Reconcile** tab and recalculate

Properties	Measured	Calculated		
Temperature (°C)	25.0000			
Pressure (atm)	1.00000			
pH	0.0	6.99650		
Alkalinity (mg HCO3/L)	0.0	2.04107		
Density (g/ml)	0.0	0.997105		
Elec Cond, specific (µmho/cm)	0.0	342.904		
Total Dissolved Solids (mg/L)	0.0	N/A		
Comp	Composition Adjustments			
Add Charge Balance (mg/L Na+1)		64.8463		

The chloride contribution is 2.04 mg/L as bicarbonate for 100 mg/L Cl<sup>-</sup> added. If 100% chloride contributed to alkalinity the maximum value would be:

$$\frac{61020 \frac{mg HCO_3^-}{mol}}{35453 \frac{mg Cl^-}{mol}} \times 100 \frac{mg Cl^-}{L} = 172.1 \frac{mg}{L} as HCO_3^-$$

Chloride has negligible effects on alkalinity for the same reason as sulfate. Both are conjugate bases of strong acids. To reach the theoretical contribution of 172.1  $\frac{mg}{L}$  as  $HCO_3^-$ , the endpoint pH would be about 5.

#### Bisulfide

- ✓ Select the Alkalinity-Bisulfide brine analysis stream
- ✓ Remove any existing concentration and add 100 mg/L bisulfide (HS<sup>-</sup>)

	Variable	Value	Balanced	
Г	Cations (mg/L)			
	Na+1	0.0	69.5108	
	Anions (mg/L)			
	HS-1	100.000	100.000	

✓ Select the **Reconcile** tab and recalculate

Properties	Measured	Calculated		
Temperature (°C)	25.0000			
Pressure (atm)	1.00000			
pH	0.0	9.19343		
Alkalinity (mg HCO3/L)	0.0	186.132		
Density (g/ml)	0.0	0.997097		
Elec Cond, specific (µmho/cm)	0.0	337.862		
Total Dissolved Solids (mg/L)	0.0	N/A		
Compo	Composition Adjustments			
Add Charge Balance (mg/L Na+1)		69.5108		

The calculated bisulfide contribution is 186.13  $\frac{mg}{L}$  as  $HCO_3^-$  for 100 mg/L added. If 100% sulfate contributed to alkalinity the maximum value would be:

$$\frac{\frac{61020 \frac{mg HCO_{3}^{-}}{mol}}{33070 \frac{mg HS^{-}}{mol}} \times 100 \frac{mg HS^{-}}{L} = 184.5 \frac{mg}{L} as HCO_{3}^{-}$$

The theoretical bisulfide ion alkalinity is  $184.5 \frac{mg}{L} as HCO_3^-$ . It has a significant impact on alkalinity. Bisulfide concentrations however are generally low in produced water. Therefore, the absolute effects are small.

A summary of all the calculation results are shown in the table below.

100 mg/L of the following ion	Initial pH	Alkalinity as mg/L HCO3
HCO3-	8.27	100.66
CO3-2	10.64	204.1
OH-	11.73	361.29
Acetate-	7.99	68.89
B(OH)4-	10.13	79.52
SO4-2	7.01	2.21
CI-	6.99	2.04
HS-	9.19	186.13

## Task 3: Alkalinity Titration Curves

The alkalinity endpoint provides a snapshot of fluid chemistry. A complete titration curve shows the system behavior across the pH profile and therefore the buffering region of different bases. In this section, we will create alkalinity titration curves for 100 mg/L of  $HCO_3^-$ ,  $CO_3^{-2}$ ,  $OH^-$ , Acetate<sup>-</sup>, and  $B(OH)_4^-$ .

The first two sections below are alternatives. Clients can either use **OLI Studio: ScaleChem** objects to create the 1N HCL reagent or use the **OLI Studio: Stream Analyzer** module.

### Task 3-1 Create the 1N HCl Reagent with OLI Studio: ScaleChem

- ✓ Add a new brine analysis Add Brine Analysis
- ✓ Name it **1N HCI-1**
- ✓ Type HCL in the neutrals section with 36,453 mg/L
- ✓ Select the show non-zero box

	Variable	Value	Balanced
	Cations	s (mg/L)	
	Anions	s (mg/L)	
	Neutral	s (mg/L)	
HCI		36453.0	36453.0

✓ Select the **Reconcile** tab then calculate

Properties	Measured	Calculated	
Temperature (°C)	25.0000		
Pressure (atm)	1.00000		
pH	0.0	0.0756504	
Alkalinity (mg HCO3/L)	0.0	0.0	
Density (g/ml)	0.0	1.01481	
Elec Cond, specific (µmho/cm)	0.0	3.33828e5	
Total Dissolved Solids (mg/L)	0.0	N/A	

It should not be surprising that the reagent pH is almost zero. HCl is a strong acid, and thus the H-Cl bond is weak, resulting in near complete dissociation. Thus, there is 1 mole H<sup>+</sup> in solution or zero pH.

✓ Save the file

#### Task 3-2 Create the 1N HCl Reagent with OLI Studio: Stream Analyzer

✓ Select the Global Streams icon in the Navigator pane



✓ Double-click the Add Stream icon in the Actions pane



- ✓ Press the <F2> key and change the name to 1N HCI-2
- ✓ Select the Units Manager icon then use the Quicklist button to pick Metric, concentration

			55 5092	Summary
Jnits Manager - 1N HC	I-2		? ×	Unit Set: Metric (moles)
Jnits Manager				Automatic Chemistry Model Aqueous (H+ ion) Databanks:
Metric	Batch ~	Moles	~	Quick List
				Metric, moles
				Metric, concentration
				Metric, molar concentration
Customize				Metric, mass fraction
Customizern				Metric, mole fraction
				SI, moles / ESP SI
				English, moles / ESP English
OK Cancel		el Apply Help	Metric, flowing, moles / ESP Metric	
	- 752			Metric, flowing, concentration
				Metric, flowing, molar concentration

✓ Press OK then enter HCI as an inflow with a concentration 36,453 mg/L

### Task 3-3 Create an Alkalinity Titration

Once we complete either of the above methods for creating the HCl reagent stream, we can proceed with the following tasks.

- ✓ Add a Mixing Water object Y Add Mixing Water
- ✓ Rename it Alkalinity Titrator

First Sec

 Change the Brine Volumes to ml (per day) by clicking a blue-colored unit and opening the Units Manager

	Composition Parameters Corrosion Inlets	
	Variable	Units
	Brine Quantity	ml/day 🛛
	Oil Quantity	ml/day
	Gas Quantity	cm3/day
Туре	Whole Fluid Quantity	m3/day E3m3/day
Srine (m3/day)		E6m3/day
ond Brine (m3/day)		ft3/day 🗸

✓ Select the bottom right corner of the Name cell and pick 1N HCL-1 as the first brine

Note: Remember that first brine is the stream that the Mixer will adjust.

✓ Set the total volume to 1000 mL/day

[	Туре	Name	Flow
	First Brine (ml/day)	1N HCI-1	1000.00
- [	Second Brine (ml/day)	~	

The 1L volume is the total liquid volume (sum of 1<sup>st</sup> and 2<sup>nd</sup> brine). In this case, the 1L will be primarily the alkalinity liquid that we will enter next. The 1N HCl reagent will be added to the Alkalinity liquid, but its volume will be relatively small. It is an imperfect example, but it serves to show another application of the *Mixing tool*. The actual flow rate is unimportant, but for realism, we will use a volume similar to laboratory conditions.

#### Task 3-4 Bicarbonate Titration Curve

✓ Select the bottom right corner of the Name cell in the Second Brine row and pick the *Alkalinity-Bicarbonate* (the original Alkalinity brine) as the second brine

	Туре	Name	Flow
Γ	First Brine (ml/day)	1N HCI-1	1000.00
	Second Brine (ml/day)	Alkalinity-Bicarbonate	

- ✓ Go to the Conditions tab
- ✓ Change the type from **Ratio** to **Flow**

Select Type		Brine Flows				
Flow		1N HCI-1 (ml/day)	Alkalinity-Bicarbonate			
FIOW	*	1000.00	0.0			
Total flow: 1000.0	00 ml/dav	800.000	200.000			
	, ,	600.000	400.000			
Channes 5		400.000	600.000			
Steps: 5	Auto Step	200.000	800.000			
		0.0	1000.00			
		5				

✓ Type 2 in the first column and first row then press tab and type 0 in the second row

Brine Flows							
1N HCI-1 (ml/day)	Alkalinity-Bicarbonate						
2.00000	998.000						
0.0	1000.00						
600.000	400.000						
400.000	600.000						
200.000	800.000						
0.0	1000.00						

✓ Change the Auto Steps amount to 20 then select the Auto Step button



The software will add the HCl at 0.1 mL increments up to 2 mL. It will also remove 0.1 mL of *Alkalinity-HCO3* volume at each step to maintain the 1000 mL volume. Consequently, the titration we are doing is not 100% correct. In an actual titration, the sample fluid volume is fixed at 100 mL. Fortunately, the HCl reagent is concentrated, and the volume added is small. This limits the displacement error to 0.2%

Select Type	Brine Flows	
Elow	1N HCI-1 (ml/day)	Alkalinity-Bicarbonate
Flow	2.00000	998.000
Total flow: 1000.00 ml/day	1.90000	998.100
. ,	1.80000	998.200
Stops: 20 Auto Stop	1.70000	998.300
Auto Step	1.60000	998.400
	1.50000	998.500
	1.40000	998.600
	1.30000	998.700
	1.20000	998.800
	1.10000	998.900
	1.00000	999.000
	0.900000	999.100
	0.800000	999.200
	0.700000	999.300
	0.600000	999.400
	0.500000	999.500
	0.400000	999.600
	0.300000	999.700
	0.200000	999.800
	0.100000	999.900
	0.0	1000.00

- ✓ Press the Calculate button
- ✓ Select the Plot tab and then select the Variables button
- Remove all existing plot variables in the Y1 Axis by highlight the Y1 axis header then select the << arrow button</li>



- ✓ Expand the Aqueous category and add HCO3-1 to the Y1 axis
- ✓ Expand the Additional Stream Parameters category and add pH-Aqueous to the Y2 axis



✓ Press **OK** and view the plot



The pH curve is the typical bicarbonate-buffering curve. The slope of the curve is shallow between pH 7 and 5.5, where bicarbonate buffering is strong. Below 5.5 pH, the curve drops sharply and has its steepest slope at about 4.5 pH.

✓ Click the View Data button

	1N HCI-1 Flow	HCO3-1	рН
	ml/day	mg/L	
1	2.00000	0.136221	3.45629
2	1.90000	0.186411	3.59319
3	1.80000	0.294252	3.79238
4	1.70000	0.662394	4.14685
5	1.60000	3.15476	4.83606
6	1.50000	8.64414	5.29927
7	1.40000	14.5983	5.55620
8	1.30000	20.6342	5.73841
9	1.20000	26.6969	5.88490
10	1.10000	32.7715	6.01163
11	1.00000	38.8520	6.12687
12	0.900000	44.9357	6.23574
13	0.800000	51.0208	6.34199
14	0.700000	57.1061	6.44885
15	0.600000	63.1903	6.55967
16	0.500000	69.2717	6.67862
17	0.400000	75.3472	6.81177
18	0.300000	81.4104	6.96974
19	0.200000	87.4421	7.17511
20	0.100000	93.3526	7.49486
21	0.0	97.6983	8.26888

- ✓ Copy the data to a spreadsheet program by holding down the left arrow, highlighting all the points and pressing <Ctrl+C>.
- ✓ Click on the View Plot button to show the plot again

🛛 🖸	View Plot	Variables	Options
-----	-----------	-----------	---------

For the following titrations, we can either add a new Mixing Water object or work from the existing object. The instructions below assume the latter.

#### Task 3-5 Carbonate Titration Curve

- ✓ Return to the **Design** | **Inlets** screen
- ✓ Replace the second brine with the *Alkalinity Carbonate* stream

Y Alkalinity Titrator								
🎻 Description 😻 Design 🛍 Plot 👼 Report								
ſ								
ets	Type Name	Flow						
Inlets	Type         Name           First Brine (ml/day)         1N HCL-1	Flow 1000.00						
Inlets	Type         Name           First Brine (ml/day)         1N HCI-1           Second Brine (ml/day)         Alkalinity-Carbonate	Flow 1000.00						

✓ Select the **Conditions** tab and change the 1N HCl flow from 2 ml to 4 ml (top cell)

Brine Flows							
1N HCI-1 (ml/day)	Alkalinity-Carbona						
4	998.000						
1.90000	998.100						

We will need twice as much acid to titrate the  $CO_3^{-2}$ 

✓ Make sure Auto steps are set at 20 and click on the Auto Step button then click on the calculate button



- ✓ Select the **Plot** tab then select the **Variables** button
- ✓ Add CO3-2 from the Aqueous categories to the Y1 Axis



✓ Press OK and view the Plot



- ✓ Click on the View Data button then copy data to a spreadsheet program
- ✓ Click on the **View Plot** button to show the plot again
- ✓ Save the file

#### Task 3-6 Hydroxide Titration Curve

✓ Return to the **Design** | **Inlets** tabs and replace the Carbonate stream with Hydroxide

Alkaliı	nity Tit	rator					
🛷 Description 😼 Design 🛍 Plot 👼 Report							
ets		Туре		Name	Flow		
Inlets	First Br	Type ine (ml/day)	1N	Name HCI-1	Flow 1000.00		

- ✓ Select the **Conditions**, tab then overwrite the first cell with 7 ml
- ✓ Press the Auto Step button and then click the calculate button

N	¥ Alkalinity Titrator								
<	🖸 De	escription 🧕 Design 🛍 Plot	5	Report					
	ets	Select Type	Brin	e Flows			Calculate 🥥		
	Ē	Flow		1N HCI-1 (ml/day)	Alkalinity-Hydroxi				
		Tatal farm 1000 00 all/day		7.00000	993.000				
	s	Total how: 1000.00 ml/day		6.65000	993.350		Summary		
		Steps: 20 Auto Step		6.30000	993.700		Unit Cate Contarts		
	dit	Addo Step		5.95000	994.050		Unit Set: <custom></custom>		

- ✓ Select the **Plot** tab then select the **Variables** button
- ✓ Remove the carbonates by double clicking on them
- ✓ Add OH- from the Aqueous section to the Y1 axis, and add pH in the Y2 axis



- ✓ Select the View Data button and copy the data to a spreadsheet
- ✓ Click on the **View Plot** button to show the plot again
- ✓ Save the file

#### Task 3-7 Acetate Titration Curve

✓ Repeat the same procedure for Acetate

¥ Alkalinity Titrator								
🎻 Description 😼 Design 🛍 Plot 👼 Report								
		2						
ets		Туре		Name	Flow			
Inlets	First B	Type rine (ml/day)	1N H	Name	Flow 1000.00			

- ✓ Select the **Conditions**, tab then overwrite the first cell with 2 ml
- ✓ Reset the Auto Steps to 20
- ✓ Press calculate then plot pH on the Y2 Axis and acetate ion (C2H3O2-1)to the Y1 axis



- ✓ Save the file
- ✓ Click on the View Data button then copy the data to a spreadsheet program

## Task 3-8 Borate Titration Curve

- ✓ Redo the calculation for Borates
- ✓ Decide upon which species are important to plot



- ✓ Click on the View Data button and copy data to a spreadsheet program
- ✓ Save the file

## Task 3-9 Sulfate Titration Curve

✓ Repeat for Sulfate



The sulfate titration calculation was taken well beyond the alkalinity endpoint in order to show the equilibrium between the  $SO_4^{-2}$  and  $HSO_4^{-2}$  species. At ~2 pH,  $SO_4^{-2}$  and  $HSO_4^{-2}$  have roughly the same concentration: this is a sulfate buffering region.

- ✓ Click on the View Data button and copy the data to a spreadsheet program
- ✓ Save the file

#### Task 3-10 Interpreting the Titration Data

- ✓ Move to the spreadsheet
- ✓ Plot the pH vs. HCl



This plot shows the buffering (pH) regions and the total buffering capacity of each weak acid. The highest buffering capacity, though not relevant to produced waters, is OH<sup>-</sup>. It's relatively low molecular weight (17 g/mol) results in more buffering per concentration (all are fixed at 100 mg/l). Its buffering region ends at about 10.5 pH (extent of shallow slope). At this pH virtually all the OH is consumed by the HCl titrant. Consequently, at typical produced water pH (between 5 and 8) no OH<sup>-</sup> buffering occurs.

✓ Plot the species concentrations vs. pH



The plot above shows the concentration impact in greater detail. It represents the concentration of free ion vs. pH for the different buffers. The red vertical line to the far left is the pH titration end point. The shaded vertical section to the right is the typical produced water pH as measured in the laboratory. From this diagram we can see that very little OH<sup>-</sup> exists in produced water between 7 and 8 pH.

The carbonate ion is dibasic (accepts two H<sup>+</sup>) and therefore has two buffering regions and endpoints. The first buffering zone exists from 10.7 to 9 pH, and the sharp pH drop reflects  $CO_3^{-2}$  depletion from solution. Few produced waters have pH above 8, and therefore  $CO_3^{-2}$  alkalinity is rarely observed. The second buffering region of  $CO_3^{-2}$  is associated with protonating  $HCO_3^{-}$ , and this second zone parallels exactly the 100 m/l  $HCO_3^{-1}$  titration curve. This second curve is the main alkalinity component in produced waters. Its existence is due to the continuous production of  $CaCO_{3(s)}$  in seawater.

The acetate buffering zone is between about 5.7 and 3.5 (end of curve). If the titration were extended, then the inflection point ~2.7 pH would have been observed. This buffering zone straddles the alkalinity endpoint, which is why it creates complications when measuring total alkalinity without an organic acid content. Organic acids are products of organics/kerogen catagenesis, which creates the fossil fuel. Therefore, it is commonly observed in produced waters. Lastly, the borates buffering region is between 10 and 8 pH with an end point at about 6 pH. Borates exist at pH's higher than the

typical produced water, but when borate concentrations are high and the laboratory measured pH approaches or exceeds 8, then this base will affect total alkalinity. Borates exist in seawater and deposit in the interstices of sediments. They are also fairly soluble (like CI and Na) and are generally found in produced waters.

The table below contains the pH and concentration data from the calculations we ran and plotted above. The shaded cells represent the regions in the titration curves that would contribute to a produced water alkalinity. At the bottom of the table is a % range value. This value represents the fraction of the species concentration that would contribute to the alkalinity.

HCO3-	1	СО	3-2	0	H-	Ace	tate-1	BOł	-14-1	SC	)4-2	н	IS-
pН	mg/l	рΗ	mg/l	рΗ	mg/l	рΗ	mg/l	pН	mg/l	рΗ	mg/l	рΗ	mg/l
3.5	0	3.2	0	2.8	0	3.4	4	3.2	0	2.8	87	3.0	0
3.6	0	3.3	0	2.9	0	3.5	6	3.2	0	2.8	88	3.1	0
3.8	0	3.6	0	3.1	0	3.7	7	3.3	0	2.8	88	3.3	0
4.1	1	4.1	0	3.3	0	3.8	10	3.4	0	2.8	89	3.4	0
4.8	3	5.2	0	3.8	0	3.9	13	3.5	0	2.9	89	3.8	0
5.3	9	5.7	0	10.3	4	4.1	17	3.7	0	2.9	90	4.9	1
5.6	15	6.0	0	10.7	10	4.2	21	3.9	0	2.9	90	5.9	7
5.7	21	6.2	0	11.0	17	4.3	26	4.5	0	2.9	91	6.2	14
5.9	27	6.4	0	11.1	23	4.4	31	8.0	5	3.0	91	6.4	20
6.0	33	6.6	0	11.2	29	4.5	37	8.4	13	3.0	92	6.5	27
6.1	39	6.9	0	11.3	36	4.6	42	8.6	21	3.1	92	6.7	34
6.2	45	7.4	0	11.4	42	4.7	48	8.8	28	3.1	93	6.8	40
6.3	51	8.8	4	11.4	49	4.8	54	9.0	36	3.2	94	6.9	47
6.4	57	9.5	14	11.5	55	4.9	59	9.1	44	3.2	94	7.0	54
6.6	63	9.7	24	11.5	62	5.0	65	9.2	51	3.3	95	7.1	60
6.7	69	10.0	34	11.6	68	5.2	71	9.4	58	3.4	95	7.3	67
6.8	75	10.1	43	11.6	74	5.3	77	9.5	66	3.5	96	7.4	73
7.0	81	10.3	51	11.6	81	5.4	82	9.6	73	3.6	97	7.6	80
7.2	87	10.4	59	11.7	87	5.6	88	9.8	79	3.8	97	7.8	87
7.5	93	10.5	66	11.7	94	6.0	94	10.0	84	4.1	98	8.1	93
8.3	98	10.6	71	11.7	100	8.0	100	10.1	89	7.0	99	9.2	99
% in range	93		0		0		63		5		1		79

Consider the following with this table: Anions are now being measured using ion chromatography. How does the alkalinity value measured relate to this ion chromatography measured ions?

#### Task 4: Effects of Temperature and Salinity on Carbonate Alkalinity

- ✓ Return to the original *Alkalinity* (or *Alkalinity-Bicarbonate*) brine
- ✓ Copy and paste it to create a new one
- ✓ Rename it Alkalinity-Bicarbonate-NaCl
- ✓ Add 23000 mg/l Na<sup>+</sup> and 35453 mg/l Cl<sup>-</sup>

👿 Alkal < Des	inity-Bicarbonate-NaCl cription 🔮 Design 🙀 F	Report				
2	Variable	Value	Balanced	Entry Options		
Ĕ	Cations (n	Units				
aF	Na+1	23000.0	23027.6	mal		
Dat				Display		
	Anions (m	Display				
	HCO3-1	100.000	100.000	Formula ~		
lcie	CI-1	35453.0	35453.0	Show Non-zero Only		

- ✓ Return to the *Alkalinity Titrator* object and select the Inlets tab
- ✓ Change the second brine to the new *Alkalinity-Bicarbonate-NaCl* brine
- ✓ Set the Max HCl to 2ml and press the Auto Steps
- ✓ Calculate, Select the Plot tab, then the Variables button
- ✓ Remove all the variables from the Y1 and Y2 axes
- ✓ Add HCO<sub>3</sub><sup>-</sup> from the Aqueous category to the Y1 Axis and pH from the Additional Stream Parameters section in the Y2 Axis



- ✓ Copy the data to the Spreadsheet and add this plot with the original **HCO**<sub>3</sub><sup>-</sup> titration plot
- ✓ Click on the *Alkalinity Titration's* Inlets tab and change the temperature to **75C**
- ✓ Calculate

✓ Plot the pH vs. HCl for the three 100 mg/l HCO<sub>3</sub><sup>-</sup> calculations (25C, 25C & 1N NaCl, and 75C & 1N NaCl).



Consider the following when viewing the plot: Under ideal conditions (25C & 0 M NaCl) the titration endpoint occurs at ~1.65 ml HCl. At more realistic conditions (1m NaCl) the endpoint occurs at ~1.6 ml HCl. This is a difference of ~3%.

## Task 5: Effects of Temperature and Salinity on Acetate Alkalinity

- ✓ Return to the *Alkalinity-Bicarbonate-NaCl* brine
- ✓ Keep the 23000 mg/I Na<sup>+</sup> and 35453 mg/I Cl<sup>-</sup>
- ✓ Frase the HCO3-1 value and add 100 mg/l acetate<sup>-1</sup>, and then **Calculate**
- ✓ Return to the *Alkalinity Titrator* and set the maximum HCl to 2 ml
- ✓ Click on Auto Step
- ✓ Recalculate to create the following pH vs. HCl plot



Consider the following when viewing the plot: Under ideal conditions (25C & 0 M NaCl) the titration endpoint occurs at ~1.1 ml HCl. At more realistic conditions (1m NaCl) the endpoint occurs at 0.75 ml HCl. A difference of ~32%!

# Summary

The purpose of this chapter was to present the quantitative chemistry of alkalinity and to expose some additional calculation features within ScaleChem. From this, we can see that additional measurements for organic acids, bisulfides, and borates can be important when considering carbonate scale risks.

## Further Reading

SPE 37277 – Alkalinity in Oilfield Waters. What alkalinity is and how it is measured. 1996. B. Kaasa and T Ostvold. 1997 SPE international symposium on Oilfield Chemistry. Houston TX.

James Drever. 1988. The Geochemistry of Natural Waters, Chapter 4: The Carbonate System and pH control. Prentice Hall.