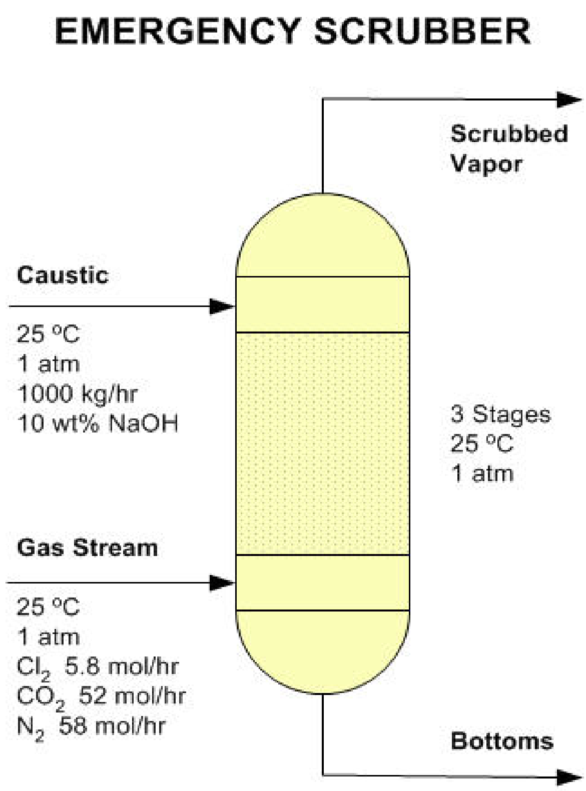
ESP FLOWSHEET SIMULATION

APPLICATION BRIEF

Emergency Chlorine Scrubber



This application brief presents the case of a scrubber that is used to remove chlorine from a process plant emergency release stream. The scrubbing agent being used is 10 wt% NaOH and there is a requirement of 90% chlorine removal.

The scrubber operates as designed until someone get's curious and wonders "*If 10% is good, wouldn't 20% be better?*"

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The Application

A scrubber has been designed to handle the emergency release from a process plant of a gas stream containing chlorine. The gas stream contains chlorine, carbon dioxide and nitrogen; the scrubbing liquid is caustic. The design specification is to remove 90% of the total chlorine.

Feed Stream		**Caustic Stream**
Cl_2	5.8 mol/hr	10-20 wt% NaOH
CO_2	52.0 mol/hr	25 ^oC
N_2	58.0 mol/hr	1 atm
25 ^oC		
1 atm		

In operation, the system has plugged. The theory is that carbonate solids are forming with CO_2 in the presence of NaOH. An aqueous chemistry analysis is really the only way to evaluate the conditions that are creating the problem. We will make use of **OLI's StreamAnalyzer** and **ESP** programs to demonstrate the chemical reactions taking place inside the scrubber that have caused the plugging problem.

Consider the Chemistry

Why does adding base remove chlorine?

The absorption of chlorine gas follows these equilibria:

$$Cl_2\ (vap) \ <====> \ Cl_2\ (aq) \qquad (1)$$

$$Cl_2\ (aq) + H_2O \ <====> \ H^+ + Cl^- + HClO^0\ (aq) \qquad (2)$$

$$HClO^0\ (aq) \ <====> \ H^+ + ClO^- \qquad (3)$$

Adding a base, such as sodium hydroxide, increases the pH. pH is defined as:

$$pH = -\log [H^+] \qquad (4)$$

If the pH increases, the concentration of the hydrogen ion must be decreasing. As the hydrogen ion decreases, the equilibria above have to shift to restore the equilibrium. Let's look at each reaction individually:

$$HClO^0\ (aq) \ <====> \ H^+ + ClO^- \qquad (3)$$

As the hydrogen ion concentration decreases, this equilibrium will dissociate more to replace the hydrogen ion. We can see that the hypochlorous ion concentration will also decrease as the hydrogen ion decreases.

$$Cl_2\ (aq) + H_2O \ <\!\!===\!\!>\ H^+ + Cl^- + HClO^0\ (aq) \qquad (2)$$

This equilibrium is more complicated. It too will shift to the right (decreasing the chlorine concentration and the water concentration) as the hydrogen ion concentration decreases. A double effect occurs because the hypochlorous ion is also decreasing.

$$Cl_2\ (vap) \ <\!\!===\!\!>\ Cl_2\ (aq) \qquad (1)$$

As the aqueous chlorine concentration decreases, the amount of chlorine remaining in the vapor phase must also decrease. This is why basic scrubbing of an acid gas works. For this case, a mole of sodium hydroxide should remove two moles of chlorine gas.

Why does the formation of sodium bicarbonate solid prevent any more chlorine from being absorbed?

Let's investigate some basic equilibria for this chemistry. When solid sodium bicarbonate is forming, this equilibrium exists:

$$NaHCO_{3(s)} \ <\!\!===\!\!>\ Na^+ + HCO_3^- \qquad (4)$$

As long as solid sodium bicarbonate is forming, the amounts of the sodium and bicarbonate ions remain constant.

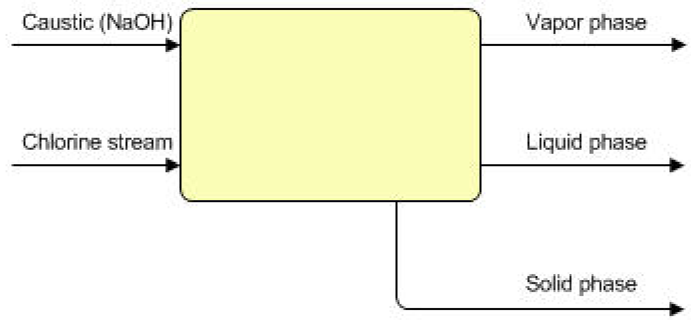
The bicarbonate ion dissociation is:

$$HCO_3^- \ <\!\!===\!\!>\ H^+ + CO_3^{2-} \qquad (5)$$

Since the hydrogen ion concentration is essentially fixed by the formation of the sodium bicarbonate, the chlorine hydrolysis (second reaction) is fixed. This fixes the VLE in the first equation. The hypochlorous acid species can not dissociate further since it is also fixed by the constant hydrogen ion. For this reason, once solids have begun forming, the pH becomes constant.

A Simple Analysis

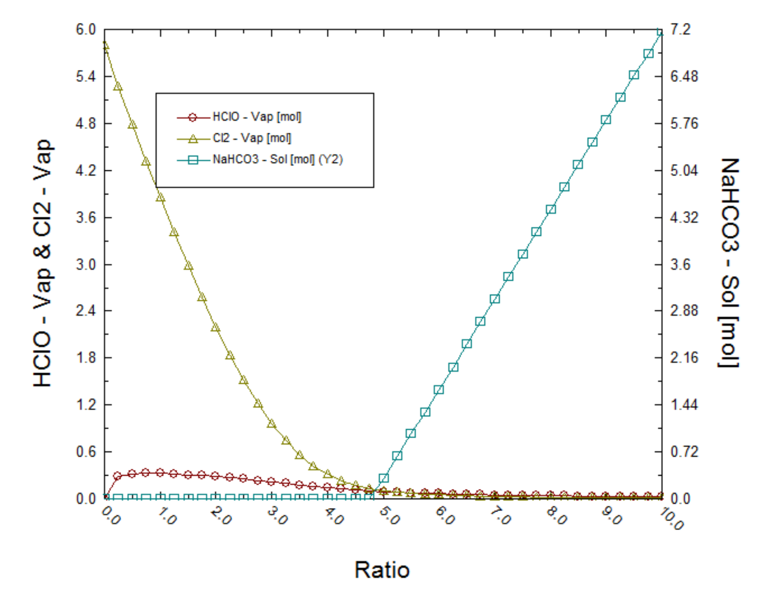
It is sometimes useful to perform a simple, one stage calculation prior to performing a multistage calculation. In this case, a simple one stage equilibrium calculation can be performed in the **OLI StreamAnalyzer** using the ***Mixed Stream*** feature. While this is not a model of a true scrubber, by varying the caustic flowrate in relation to the gas stream and also varying the NaOH concentration, we can get a qualitative view of the chemistry:



- Viewing the calculation results shows that some of the Cl_2 in the feed stream reacts to form HClO, as our analysis of the chemical equilibrium demonstrates. Most of the HClO leaves the system in the liquid phase, although a small amount would pass out of the scrubber in the vapor phase. The chlorine in the HClO would have to be taken into account in the design to meet the design requirement of 90% total chlorine removal.

- Viewing a plot of the amount of chlorine in the vapor phase vs. NaOH reveals that total chlorine (Cl_2 + HClO) reaches close to the 0.58 moles target value at around 3.75 NaOH ratio. This is equal to about 197 mol/hr of 10% NaOH.

- Viewing solids formation in the liquid phase vs. NaOH reveals that solids begin forming at about 4.75 NaOH ratio. This is equal to about 250 moles of 10% NaOH. This is above the amount required to reach the 0.58 moles of chlorine allowed in the scrubbed gas stream.



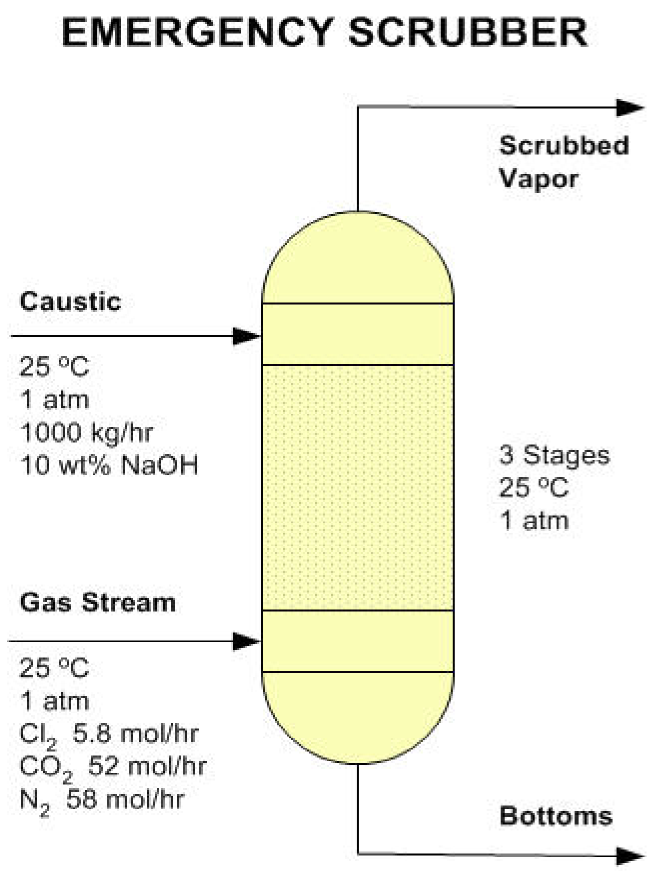
This simple 1 stage calculation gives us a good starting point for estimates in the ESP simulation and allows us to view the effect of NaOH flowrate on both chlorine removal and solids formation in an convenient format.

Formulating the Process

In **ESP** the scrubber can be simulated as a multi-stage absorber that contains a feedback controller to adjust the amount of caustic fed to the top of the vessel to achieve the desired 90% total chlorine removal. This means that the flowrate of the caustic stream will be varied until the scrubbed vapor stream contains 0.58 mol of Cl_2 + HClO (10% of the 5.8 mol of Cl_2 in the feed gas).

The stripper input conditions are:

Feed Stream		Caustic Stream
Cl_2	5.8 mol/hr	10-20 wt% NaOH
CO_2	52.0 mol/hr	25 ^oC
N_2	58.0 mol/hr	1 atm
H2O	0.0 mol/hr	
HClO	0.0 mol/hr	
25 ^oC		
1 atm		



When the simulation is complete, the results reveal that the design specification of 0.58 mol/hr Cl_2 + HClO in the ***Scrubbed Vapor*** stream has been achieved. The caustic stream flowrate has been adjusted to 154.4 mol/hr to meet this requirement.

Our other concern was to avoid forming solids in the scrubber. While **ESP** does not calculate any actual solids in a column, a saturation index, also known as a scaling tendency, is calculated. The 3 most likely solids are:

Stage	$NaHCO_3$	$Na_2CO_3.1H_2O$	NaCl
3	0.4190	0.0005	0.0526
2	0.1900	<.0001	0.0838
1	0.2539	<.0001	0.0927

The scaling indices of some of the solids are less than 0.0001. This means that those solids are not likely to form and plug the scrubber.

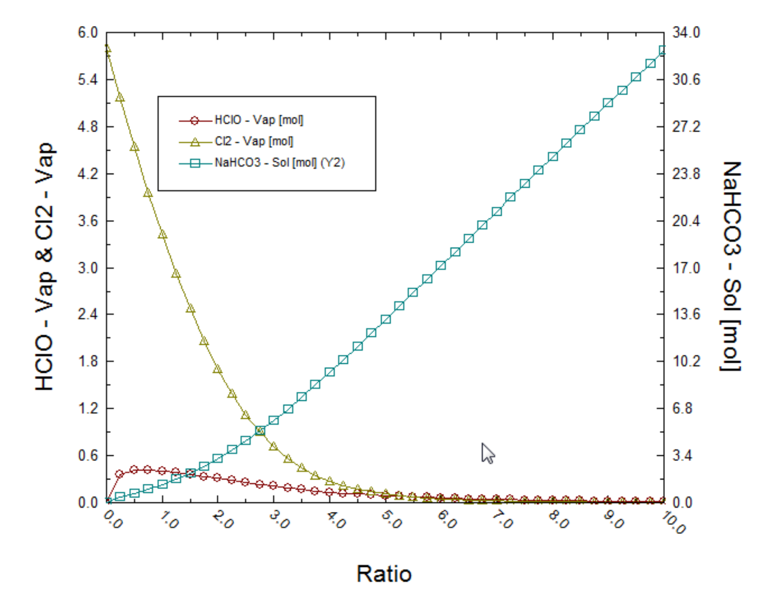
Other solids, like $NaHCO_3$, have a scaling index that is between 0.0001 and 1. These components will become more of a concern as the scaling index approaches 1.0.

Overall, **ESP** has shown us that 90% chlorine removal from the process stream is achieved with 2810 g/hr of 10 wt% NaOH solution in a 3 stage scrubber.

If 10% is good, wouldn't 20% be better?

In actual practice, an operator introduced 20 wt% NaOH to the scrubber instead of 10 wt%. Will using 20 wt% NaOH give better chlorine gas scrubbing results? Let's see what **StreamAnalyzer** and **ESP** will predict with this change.

In **StreamAnalyzer**, we will mix the same vapor stream with a 20 wt% NaOH liquid stream for a simulation of a simple, 1-stage scrubber block. The results are **very** revealing!



The $NaHCO_3$ line shows that solids will begin forming immediately as the gas comes into contact with 20 wt% NaOH! We don't even need to look at what NaOH rate will achieve the 90% chlorine removal design spec.

Now let's examine the **ESP** analysis of this case:

Stage	$NaHCO_3$	$Na_2CO_3.1H_2O$	NaCl
3	2.7250	0.0498	0.3559
2	2.0486	<.0001	0.6206
1	3.1202	<.0001	0.6776

The scaling tendency numbers for $NaHCO_3$ are above 2 at all stages and even the numbers for NaCl are approaching 1.0.

ESP and **StreamAnalyze**r both confirm that changing to 20 wt% NaOH will cause solids formation to occur at all flowrates of caustic and on all stages of the scrubber. This verifies the field experience that the scrubber operates fine with 10 wt% NaOH, but plugs using 20 wt% solution. It also provides a firm answer to the question "If 10% is good, wouldn't 20% be better?" – **NO!!!**