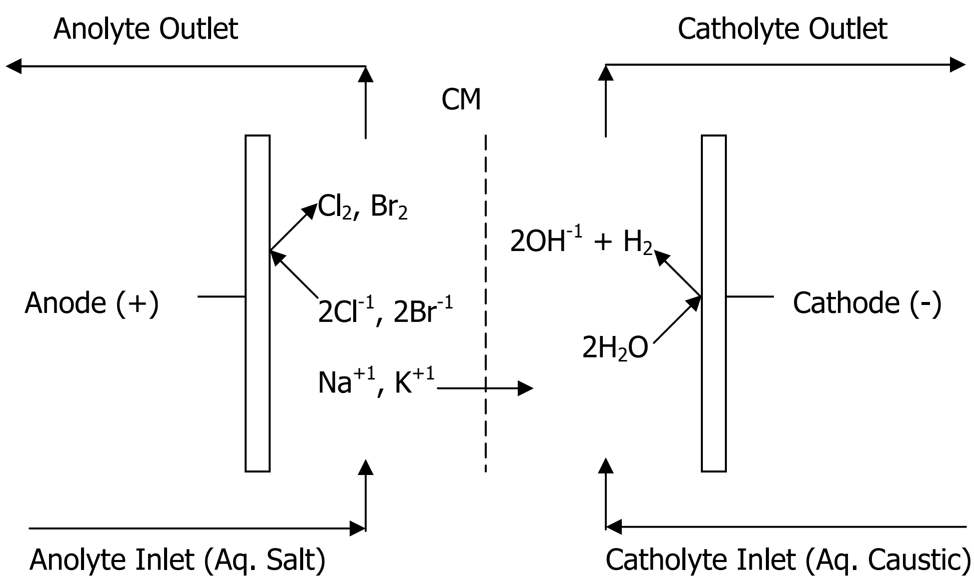
ESP FLOWSHEET SIMULATION
APPLICATION BRIEF
Chlor-Alkali Simulation

Revised April 10, 2012[1]

The anode in an electrochemical cell is the strongest oxidizer known, as it is fully capable of taking an electron away from fluoride ion to produce fluorine gas ($2F^{-1} \rightarrow F_{2(g)}$.+ $2e^-$, E_o=3.077v). In fact, this reaction is practiced on an industrial scale with electrochemical cells. Likewise, the cathode is the strongest reducing agent known. It is only natural that OLI would make this Oxidation/Reduction tool available to its users. The ESP Electrolyzer Block models the behavior of a typical chloralkali membrane cell.



CM = Cation Exchange Membrane

Figure 1 Schematic of the OLI Electrolyzer block

[1] Using OLI ESP version 8.3.9

Contents

The Application

Your cell room is running fine right now. The Sales Dept. just called to see if you can increase the plant capacity from 41 tonne/day (45 ton/day) Cl_2 production to 45 tonne/day (49.5 ton/day). You have 20 cells with an electrode area of 21 m^2 each running at a current density of 3,543.6 amp/m^2 at an anode current efficiency of 96% and a cathode current efficiency of 91%. The cell membranes transport an average of 4.1 moles of water per mole of cation transported. You have room for two more cells on the plant floor. This is a good time to try out that new ESP block you got with the latest update from OLI. How will you increase the plant capacity?

Electrolyzer Theory and Implementation

The electrochemical cell is divided with a cation exchange membrane. A cation exchange membrane is a cross-linked perfluorinated polymer backbone with sulfonic acid groups attached to it. The acid functionality provides discrete channels for cations to migrate through the polymer matrix while blocking the passage of anions. A divided cell has separate flow channels for a fluid (the Anolyte) to come in electrical contact with the anode and the cathode (the Catholyte). A number of these flow channels are often stacked together and connected to common headers much like a plate and frame heat exchanger.

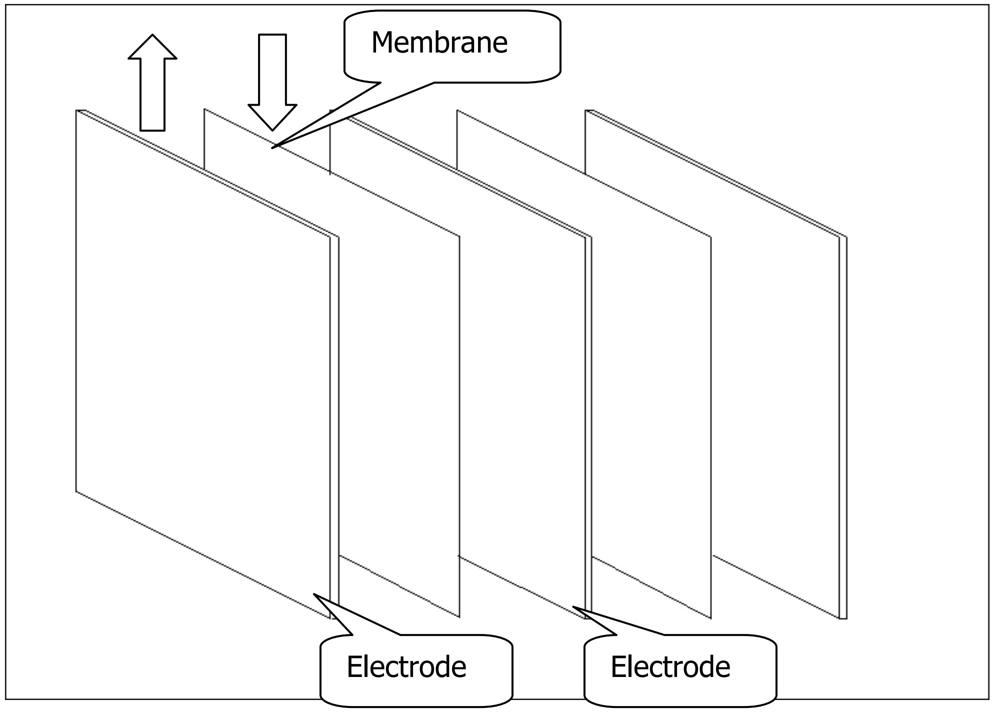


Figure 2. Repeating Cell Components

A potential applied to the electrodes of an electrochemical cell establishes an electrostatic attraction for cations to the cathode and away from the anode. Likewise, anions are attracted to the anode and repelled by the cathode. The movement of ions in the Anolyte and Catholyte is an electrical current. Anions that come in contact with the anode are subject to electrochemical reaction if the anode potential is sufficiently high. Similarly, for cations that come in contact with the cathode. Modern membrane cells used in the Chloralkali Industry are constructed in this fashion. The ESP Electrolyzer Block accurately models the behavior of Membrane Chloralkali Cells in common industrial use.

The OLI chemical and thermodynamic model allows for accurate calculation of the equilibrium conditions in both compartments of an electrochemical cell. The Electrolyzer Block is able to correctly predict the behavior of both the Anolyte and Catholyte for the limited species it was designed to address. The following discussion will help you supply this ESP block with reasonable input data and provide you with a basis for verifying its accuracy. Sodium Hydroxide and Chlorine will be used as an example but the principles are equally valid for other caustics and halogens.

Chloralkali anode reactions

The anolyte is normally a salt solution just below its saturation point. The anode is coated with a catalyst to suppress the decomposition of water and facilitate the formation of halogen. The anolyte is usually acidified to about pH=2 to suppress the formation of chlorates (bromates, etc.) and protect the anode catalyst from alkaline conditions. For example, chloride ion in the anolyte is attracted to the anode. When it touches the anode, it surrenders an electron and forms chlorine gas bubbles on the surface, which are then swept away by the flow of Anolyte.

$$Cl^{-1} \rightarrow \frac{1}{2} Cl_{2(g)} + e^{-} \quad (1.3604 \text{ volt @ 25 °C})$$

Note that each mole of chloride ion reacts to form one mole of electrons so this is a one-electron process. Unfortunately, there is a competing side reaction since even saturated salt solutions contain more moles of water than salt. Water is Thermodynamically favored to decompose at the anode to produce oxygen and hydrogen ion in a two-electron process.

$$H_2O \rightarrow 2\, H^{+1} + \frac{1}{2} O_{2(g)} + 2\, e^{-} \quad (1.2291 \text{ volt @ 25 °C})$$

The anode catalyst suppresses this reaction. The ratio of the chloride ion process to the total amount of current used by the anode (to form chlorine and decompose water) is the anode current efficiency (ς). Modern anode materials are typically between 95% and 97% efficient. Clearly, the anode will produce some oxygen gas. Enough anolyte must be provided to keep a high concentration of chloride ion over the entire anode surface. The anolyte salt concentration therefore typically drops only a few percent in the cell. Chloralkali Cells are designed to operate at about 90 °C to limit the solubility of the halogen in the aqueous anolyte solution. Meanwhile, the corresponding sodium ion moves toward the cathode and crosses the cation exchange membrane.

CHLORALKALI CATION EXCHANGE MEMBRANE TRANSPORT

Cations, especially hydrogen ions, are able to pass through the polymer matrix of the cation exchange membrane. However, each cation is solvated by more than one water molecule and these waters of hydration pass through the cationic membrane as well. Each cation drags from two to six water molecules along with it depending on their size and charge but somewhere around four is common.

The cation exchange membrane is positioned between the anolyte and catholyte and must keep them from mixing. The catholyte is strongly alkaline and would damage the catalytic coating on the anode while the anolyte is strongly acidic. The cations must be able to pass through the cation exchange membrane from the acidic anolyte to the caustic catholyte without precipitating. If they do, the precipitation will probably occur inside the membrane structure and cause permanent damage to the membrane. This is why industrial chloralkali facilities spend so much effort removing calcium/magnesium from their feed brine. The ESP Electrolyzer Block can predict this problem and will warn the user if a species gets too close to saturation.

BACK MIGRATION ACROSS THE MEMBRANE

The anolyte contains a high concentration of chloride ion and the catholyte has a high concentration of hydroxide ion. The cation exchange membrane separates these two solutions. Sulfonic acid moieties in the membrane polymer attempt to block the passage of anions. However, a small amount of chloride ion finds its way into the catholyte and a small amount of hydroxide ion gets into the anolyte. Both of these leakages are referred to as "Back Migration" of anions across the cation membrane. The degree of back migration depends on the condition and construction of the cation exchange membrane, the concentration gradients and the type of anion. If chloride ion leaks into the catholyte, the caustic (NaOH in this example) will be contaminated with salt (NaCl). Modern membrane materials used in the chloralkali industry are able to keep this contamination to a few tens of ppm while producing 30% to 33% NaOH. If hydroxide ion back migrates into the anolyte, it combines with dissolved chlorine gas to produce hypochlorite.

$$OH^{-1} + Cl_{2(aq)} \rightarrow H^{+1}\ Cl^{-1} + ClO^{-1}$$

The ESP Electrolyzer Block will correctly predict this behavior if the chemistry model is constructed properly. Do not turn on the REDOX option.

The Electrolyzer Block will account for hydroxide back migration from the Cathode Efficiency and predict the formation of hypochlorite and chlorate in the anolyte. In order to understand the importance of back migration, let us examine the cathode reactions.

CHLORALKALI CATHODE REACTIONS

The Thermodynamic potential for the decomposition of water to form hydrogen gas and hydroxide ion at the cathode is very low so it is far more likely to proceed than other possible cathode reactions in a chloralkali application.

$$H_2O + e^- \rightarrow \tfrac{1}{2}\ H_{2(g)} + OH^{-1} \quad (-0.8280 \text{ volts @ } 25\ °C)$$

Thus, sodium ion transported across the membrane to the catholyte is joined by hydroxide from the cathode surface to produce NaOH. However, if hydroxide ions were to be neutralized by hydrogen ion transporting across the membrane or if hydroxide back migrates into the anolyte, the cathode reaction is not 100% efficient in the formation of hydroxide. Recall that the undesired side reaction from the anode produces hydrogen ion, which impacts the cathode. Cationic hydrogen can easily migrate across the cation exchange membrane.

Anodic Side Reaction

$$H_2O \rightarrow 2\ H^{+1} + \tfrac{1}{2}\ O_{2(g)} + 2\ e^-$$

Cathodic Side Reaction

$$H^{+1} + OH^{-1} \rightarrow H_2O$$

Hydroxide ion that back migrates into the anolyte is lost to the catholyte product. It also reacts with dissolved chlorine gas in the anolyte to form hypochlorite in an unwanted side reaction. The ratio of hydroxide to hydrogen gas produced from the cathode compartment is the cathode current efficiency (η). This may be an unfortunate designation as the cathode's hydrogen efficiency is 100% and the cathode has little to do with the loss of hydroxide ion from the catholyte. Modern Chloralkali membranes and anode catalysts allow the cathode current efficiency to run between 85% and 94%. The anode and cathode current efficiencies are related so that the cathode efficiency can never be higher than the anode efficiency.

One additional point should be made about the relative size of the anolyte and catholyte streams. The anolyte composition may go from 23% NaCl at the inlet to about 21.5% at the outlet. That means the anolyte feed stream is big compared to the amount of NaCl converted. This is required to keep a high concentration of chloride ion near the anode. However, the cell membrane cannot withstand large differences in pressure between the anolyte and catholyte so it is not unusual for the catholyte to be a large stream as well. The catholyte inlet may be 32% NaOH and the outlet may get as high as 33% NaOH depending on the performance of the membrane.

CHLORALKALI MASS BALANCE CALCULATIONS

The rate of conversion in an electrochemical cell is governed by the amount of current that passes between the cathode and anode according to the following relationship.

$$Q = n \Im e$$

Where: Q = cell current in amperes (1 amp = 1 coulomb/sec)
n = molar rate of reaction (moles/sec)
$\Im$ = Faraday's Constant (96485.3 coulomb/equivalent)
e = number of equivalents per mole of reactant or number of electrons involved in the reaction per mole of reactant (equivalents/mole)

Then if we define the efficiencies as follows:
ζ = Anode Current Efficiency (fraction)
η = Cathode Current Efficiency (fraction)
f = Membrane Water Transport Factor (moles of water transported across the membrane per mole of cations transported)

We can summarize the performance of our example chloralkali cell as follows:
For every 100 moles of electrons that passes through the cell:

100*η moles of NaOH are formed in the catholyte.

100 moles of Hydrogen atoms or 50 moles of $H_{2(gas)}$ is formed in the catholyte.

100*ζ moles of Chlorine atoms or 50*ζ moles of $Cl_{2(gas)}$ is formed in the anolyte.

100*(1-ζ)/2 moles of Oxygen atoms or 50*(1-ζ)/2 moles of $O_{2(gas)}$ is formed in the anolyte. Formation of oxygen is a two-electron process.

100*(1-η) moles of hydroxide ion is lost from the catholyte.

100*(1-ζ) moles of hydrogen ion combines with back migrating hydroxide ions to form water in an unwanted side reaction.

100*(ζ-η) moles of hypochlorite is formed in the anolyte.

The ESP Electrolyzer Block performs all of these calculations.

BLOCK Computations

$\mathbf{I_C}$ = Current (amp) = Current Density (amp/m^2) * Area (m^2)
e^- = Electrons (mole/hr) = (Current (amp) * 3600 (sec/hr))/($\Im$ (amp-sec/equiv) * 1 equiv/mole)

ANOLYTE STREAM

Consumed by Reaction:

H_2O	$\left(\frac{1-\zeta}{2}\right)$ e^- mole/hr
Salt Conversion	$\zeta\ e^-$

Removed by Transport:

H_2O	$f\ \eta\ e^-$

Produced by Reaction:

Halogen (Cl_2, Br_2)	$\left(\frac{\zeta}{2}\right)$ e^-
O_2	$\left(\frac{1-\zeta}{4}\right)$ e^-

Produced by OHION Back Migration:

Hydroxide in the Anolyte (NaOH, KOH)	$(\zeta - \eta)\ e^-$
H_2O formed in the anolyte.	$(1 - \zeta)\ e^-$

CATHOLYTE STREAM

Consumed by Reaction:

H_2O	1 e^- mole/hr

Produced by Reaction:

Hydroxide (NaOH, KOH)	$\eta\ e^-$
H_2	½ e^-

Added by Transport from the Anolyte:

H_2O	$f\ \eta\ e^-$

EXAMPLE MATERIAL BALANCE

For NaCl:

Let $\mathbf{e}^-$ = 1 mole/hr

Anolyte In:

$$\left(\frac{1-\zeta}{2}\right)H_2O + \zeta NaCl + f\eta H_2O$$

Anolyte Out

$$\left(\frac{\zeta}{2}\right)Cl_2 + \left(\frac{1-\zeta}{4}\right)O_2 + (\zeta - \eta)\ NaOH + (1 - \zeta)H_2O$$

Catholyte In:

$1\ H_2O$

Catholyte Out:

$\eta NaOH + ½H_2 + f\eta H_2O$

Total In (Anolyte In + Catholyte In):

H2O:	$\left(\frac{1-\zeta}{2}\right) + f\eta + 1 = \frac{3}{2} - \frac{\zeta}{2} + f\eta$
NaCl:	ζ

Elements In:

H:	$3 - \zeta + 2\ f\eta$
O:	$\frac{3}{2} - \frac{\zeta}{2} + f\eta$
Na:	ζ
Cl:	ζ

Total Out (Anolyte Out + Catholyte Out):

Cl_2	$\frac{\zeta}{2}$
O_2	$\frac{1-\zeta}{4}$
NaOH	$\zeta - \eta + \eta = \zeta$
H_2O:	$1 - \zeta + f\eta$
H_2	½

Elements Out:

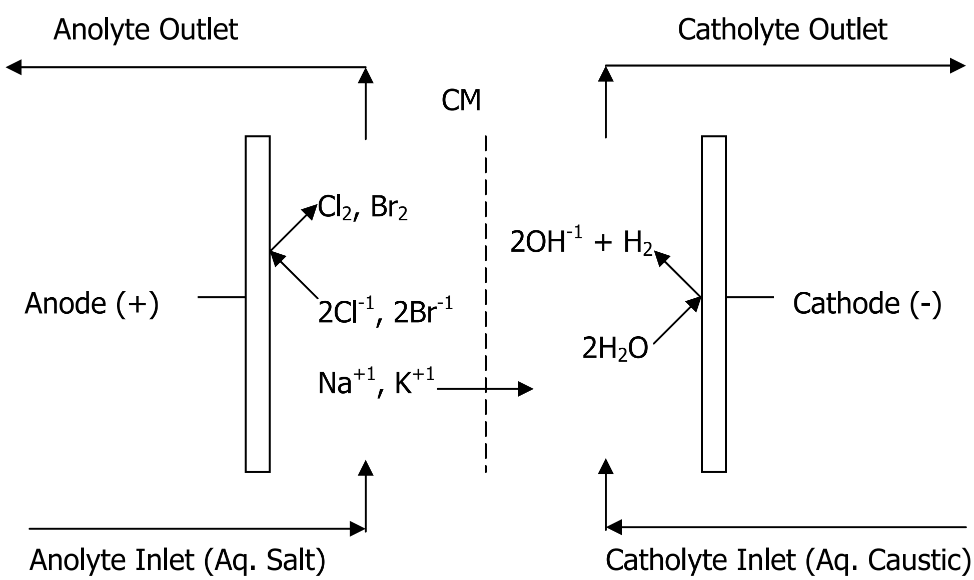
H:	$\zeta + 2 - 2\zeta + 2f\eta + 1 = 3 - \zeta + 2\ f\eta$	√ Balanced
O:	$\frac{1-\zeta}{2} + \zeta + 1 - \zeta + f\eta = \frac{3}{2} - \frac{\zeta}{2} + f\ \eta$	√ Balanced
Na:	ζ	√ Balanced
Cl:	ζ	√ Balanced

Block computation Options

Overview

The Electrolyzer block has several options which affects the calculations. The block can react chlorides or bromides and may use Potassium or Sodium ions. The user can also specify whether the area is calculated or the salt conversion is calculated.

Specification options



CM = Cation Exchange Membrane

Figure 3 Schematic of the OLI Electrolyzer block

1) Specify Current Density and Electrode Area; Compute Conversion

   or

2) Specify Conversion and Current Density; Compute Electrode Area.

Reactions:

Anode: $Cl^{-1} \rightarrow \frac{1}{2} Cl_2 + e^-$

$Br^{-1} \rightarrow \frac{1}{2} Br_2 + e^-$

Cathode: $H_2O + e^- \rightarrow \frac{1}{2} H_2 + OH^{-1}$

Parasitic Side Reactions:

$H_2O \rightarrow \frac{1}{2} O_2 + 2 H^+$
$H^+ + OH^- \rightarrow H_2O$

Input Information

- Exit Temperature Option
  1) Isothermal and Isobaric (Inlet = Outlet)
  2) Temperature and Pressure Specified

- Computation Option
  1) Specify Current Density ($Amps/m^2$) and Electrode Area (m^2); Compute Conversion
  2) Specify Conversion (Mass rate of Salt to be removed from the Anolyte Inlet) and Current Density ($amps/m^2$); Compute Cell Current.

- Current Density (amp/m^2) *(default = 3,000) (max ~ 6,000, min ~ 1,000, normal ~ 4,000 in chloralkali applications such as this.)*
- Anode Current Efficiency (fraction) *(default = 0.95)*
- Cathode Current Efficiency (fraction) *(default = 0.88)*
- Water Transport Factor (Moles of Water transported across the membrane per mole of cation transported) *(default = 4)*
- Choice of Salt:
  1) NaCl
  2) KCl
  3) NaBr
  4) KBr

Example 1 – Existing installation[2]

Chemistry Model

We start by modeling the existing cell room. Start ESP and enter your species into a chemistry model. Your input species should be as follows:

H2O
NACL
HCL
NAOH
CL2
O2
H2

Complete the model generation process as you would normally.

[2] This is using Example file CHLORAL2.BIN

Do not use Oxidation / Reduction!

ESP Process Build – Pre-build calculations

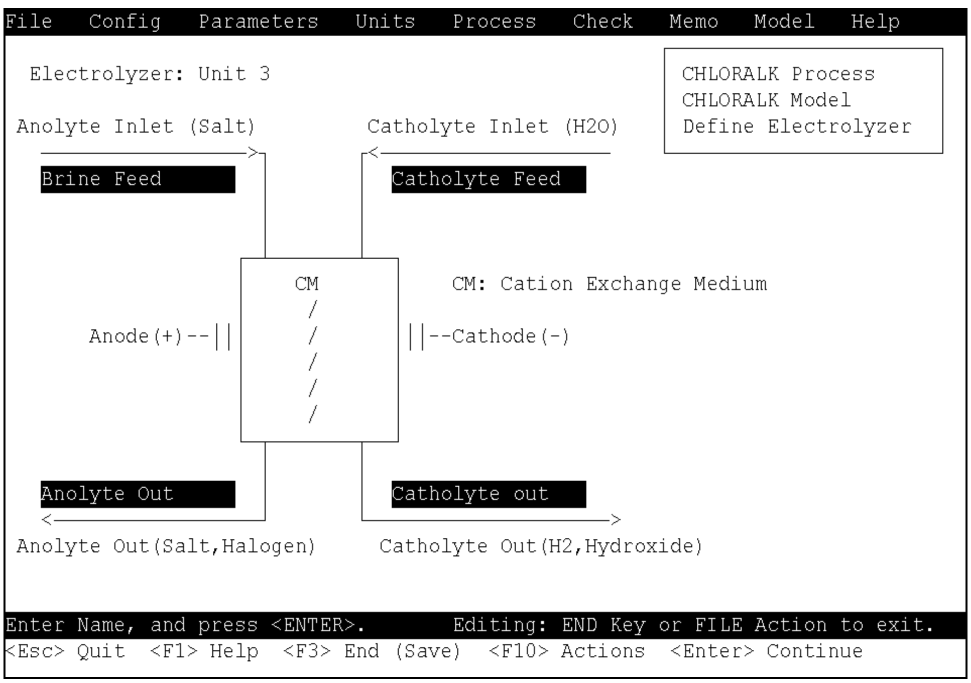
The existing plant has some non-ESP related data. We must take a few moments to convert this data into more ESP friendly values.

The Anolyte Input stream pumps provide about 242 m^3/hr (1064 gpm) to the cells. This corresponds to approximately 270940 Kg/hr. The area of each cell is 21 m^2 and there are 20 cells for a total of 420 m^2.

The other parameters are stated at the beginning of the document.

ESP Process Build – data entry

Open Process build and then select an Electrolyzer block from the Environmental blocks grouping. Create the following streams in the block:



Enter the stream compositions for the two inlets

Anolyte Inlet (Salt): Brine Feed
Temp: 87 °C
Pressure: 130 kPa
Total Flow: 270,940.0 kg/hr
H2O: 208,606.0 kg/hr
NaCl: 62,310.9 kg/hr
HCl: 23.1 kg/hr

Catholyte Inlet (H2O): Catholyte Feed
Temp: 85 °C
Pressure: 130 kPa
Total Flow: 269,490.0 kg/hr
H2O: 183,927.0 kg/hr
NaOH: 85,563.1 kg/hr

After all the streams are named, enter the operating parameters for this problem as follows:

Exit Temperature; Set Temperature = 91 °C
Computation Option = Specify Area; Compute Salt Conversion
Choice of Salt = NaCl.
Operating Conditions:

Current Density	= 3543.6 amp/m2
Area	= 420 m2
Anode Efficiency	= 0.96
Cathode Efficiency	= 0.91
Water Transport Factor	= 4.1

The model is now ready to run. The results will look something like Table on the following pages. A quick check of the results table will confirm the mass balance closes to within 0.4 ppm. Notice the amount of chlorine produced by the cells. 1699 kg/hr is indeed about 40.8 tonne/day. This confirms that we are properly modeling the existing installation.

Table 1 Existing current density

			Chlorine Header		Hydrogen Header	
Stream	Brine Feed	Catholyte Feed	Anolyte Out	Anolyte Out	Catholyte out	Catholyte out
Phase	Liquid-1	Liquid-1	Liquid-1	Vapor	Liquid-1	Vapor
Temperature, C	87	85	91	91	91	91
Pressure, kPa	130	130	130	130	130	130
pH	2.30	14.07	4.00		13.93	
Total mol/hr	12646214	12348710	12371556	45226.6	12539355	39242.9
Flow Units	kg/hr	kg/hr	kg/hr	kg/hr	kg/hr	kg/hr
H2O	208606.19	203196.33	204520.60	372.67	186451.66	206.85
HCL	23.10		23.10	0.00		
NACL	62310.71		59196.95			
NA2O		66293.67				
CL2			189.22	1699.07		
HCLO				1.26		
O2			0.03	17.74		
NAOH			110.09		87584.33	
H2					0.01	55.96
Total kg/hr	270940	269490	264040	2090.73	274036	262.817
Volume, m3/hr	241.724	207.874	236.869	1043.11	211.37	913.62
Enthalpy, cal/hr	-8.82E+11	-9.18E+11	-8.61E+11	-1.17E+09	-9.31E+11	-644894000
STD Liq Vol, m3/hr	246.911	231.765	241.112	1.46475	235.415	1.00053
Density, kg/m3	1120.86	1296.41	1114.71	2.00432	1296.48	0.287666
Vapor fraction				1		1
Solid fraction						
Liquid-2 fractio						
Osmotic Pres, kPa	36205.7554	127593.5149	35116.5116		127881.2779	
Redox Pot, volts						
Surf Tension N/m						
Ionic Str, Molal	5.11406	11.6309	4.96582		11.7444	

Example 2 – Changing the existing installation[3]

Can we achieve our desired production rate by increasing the current density? We are not going to change the chemistry model for this example, only we will rerun the calculation at a higher current density to see if existing cells will handle the new load. An off-line calculation indicates that the new current density should be 3,897.9 amp/m^2. The cells should be able to handle a current density less than 4,000 amp/m^2. All of the block operating parameters remains the same except the following:

Operating Conditions: Current Density = 3897.9 amp/m2

The results of this simulation should look something like Table 2 below. Sure enough, the cells will produce 1868.5 kg/hr or 44.8 tonne/day of Chlorine. We are now predicting that we will produce approximately 45 tonne/day of chorine. This might be acceptable to the sales department.

Table 2 Increased current density

			Chlorine Header		Hydogen Header	
Stream	Brine Feed	Catholyte Feed	Anolyte Out	Anolyte Out	Catholyte out	Catholyte out
Phase	Liquid-1	Liquid-1	Liquid-1	Vapor	Liquid-1	Vapor
Temperature, C	87	85	91	91	91	91
Pressure, kPa	130	130	130	130	130	130
pH	2.30	14.07	4.05		13.93	
Total mol/hr	12646214	12348710	12344067	49775.3	12558515	43152
Flow Units	kg/hr	kg/hr	kg/hr	kg/hr	kg/hr	kg/hr
H2O	208606.19	203196.33	204112.00	410.46	186704.72	227.27
HCL	23.10		23.10	0.00		
NACL	62310.71		58885.54			
NA2O		66293.67				
CL2			208.36	1868.49		
HCLO				1.56		
O2			0.03	19.51		
NAOH			120.97		87786.27	
H2					0.01	61.56
Total kg/hr	270940	269490	263350	2300.03	274491	288.826
Volume, m3/hr	241.724	207.874	236.33	1148.02	211.684	1004.63
Enthalpy, cal/hr	-8.82E+11	-9.18E+11	-8.59E+11	-1.29E+09	-9.33E+11	-708514000
STD Liq Vol, m3/hr	246.911	231.765	240.532	1.61156	235.78	1.10031
Density, kg/m3	1120.86	1296.41	1114.33	2.00347	1296.7	0.287494
Vapor fraction				1		1
Solid fraction						
Liquid-2 fractio						
Osmotic Pres, kPa	36205.75542	127593.5149	34981.95199		128059.6099	
Redox Pot, volts						
Surf Tension N/m						
Ionic Str, Molal	5.11406	11.6309	4.95101		11.7556	

[3] This is example file CHLORAL3

Example 3 – Increased salt conversion[4]

The Process Block Results show that for the first scenario the cells convert 5% of the available salt in the anolyte stream. Converting more salt will increase our yield. We will now rerun the simulation to convert 6.05% of the available salt. All other parameters remain the same as the first run except the following (*make sure you reset the current density):*

Operating Conditions: Current Density = 3897.9 amp/m2
Computation Option = Specify Conversion. Salt Conversion = 0.0605

A review of the **Process Stream Results** for the ***Anolyte Out*** stream shows that we still have 2055 Kg/hr of chlorine being produced (49.3 tonne/day ~ 50 tonne/day).

In this example, the information we need is stored in the block results. Select **Process Block Results** from the Process Analysis dialog. Then select the only block present – the electrolyzer block.

There is a wealth of information in this block. The section we are interested in is the ***Effective Transfer Area (m^2) = 462.002***.

Notice that the required area is 462 m^2 or two additional cells (420+2*21 m^2). So, the increased production could be met by installing two additional cells.

Conclusion

ESP allows the user to quickly model an existing facility or perform "What if" scenarios. In this particular case, we can achieve the salt conversion we desire by increasing the current density or by adding more cells.

[4] This is example file CHLORALK