E-Chem Education: a crash course in electrochemical engineering for caustic soda plant design

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The capstone chemical engineering senior process design course at Penn State in Spring 2023 tasked students to design a caustic soda process to partially meet the global demand for commoditized sodium hydroxide. This article disseminates our experience teaching senior chemical engineering students the core tenets of electrochemical engineering in a single class period for designing an electrolytic caustic soda process. In this E-Chem Education article, we relate key concepts found in chemical engineering (such as sizing up a reactor volume), which chemical engineering seniors are adept with, to electrochemical engineering principles (e.g., current density, voltage, and membrane electrode assembly area) for sizing up and costing out a chlor-alkali electrolyzer. Furthermore, we also discuss alternative electrolyzer designs outside the traditional chlor-alkali process, such as oxygen depolarized cathode (ODC) chlor-alkali and bipolar membrane electrodialysis (BPMED), for caustic soda production and the pros and cons for the alternative process designs.

Most ECS members came to the field of electrochemistry/ electrochemical engineering via research in topic areas outside chlor-alkali and electrowinning aluminum. However, the said two processes are the most mature in the field of industrial electrochemical engineering and are practiced at scale. Hence, most ECS members only come to learn about the two industrial processes when taking a formal electrochemical engineering course (or having to teach it). As an aside, I (Chris Arges) am a big fan of the science fiction writer Any Weir, who wrote The Martian, Project Hail Mary, and Artemis. In the latter book, Artemis, which named for the moon colony where the story takes place, an electrowinning process converts anorthite, an abundant moon mineral, to oxygen and aluminum. The oxygen enables the humans in the colony to breathe and the aluminum is used for constructing buildings. Because of the massive effort to decarbonize the global economy by 50% in 2030 and have net-zero emissions by 2050, there is a tremendous effort to electrify industrial processes – especially hard to abate CO_2 emission processes such as fertilizer production, steel manufacturing, and concrete production. Whether it is imagining moon colonies or taking on dire global challenges, giving soon to be process engineers a foundation in electrochemistry is useful.

The CHE 470 Senior Capstone Design at Penn State tasked 121 chemical engineering seniors to design a chlor-alkali process (**Figure 1**) for their caustic soda plant. This plant was required to deliver 525 kilo-tonnes per annum (ktpa) of sodium hydroxide. The key learning objectives for the course were: 1) hierarchical design to break large projects with hundreds of degrees of freedom (DOF) into smaller chunks with a more manageable number of DoF, 2) optimizing the plant based on net present value (NPV) rather than on conversion or other technical measures,

3) analyzing the tradeoff of OpEx and CapEx, and 4) integrating previous technical knowledge together, and finding new technical knowledge as needed.

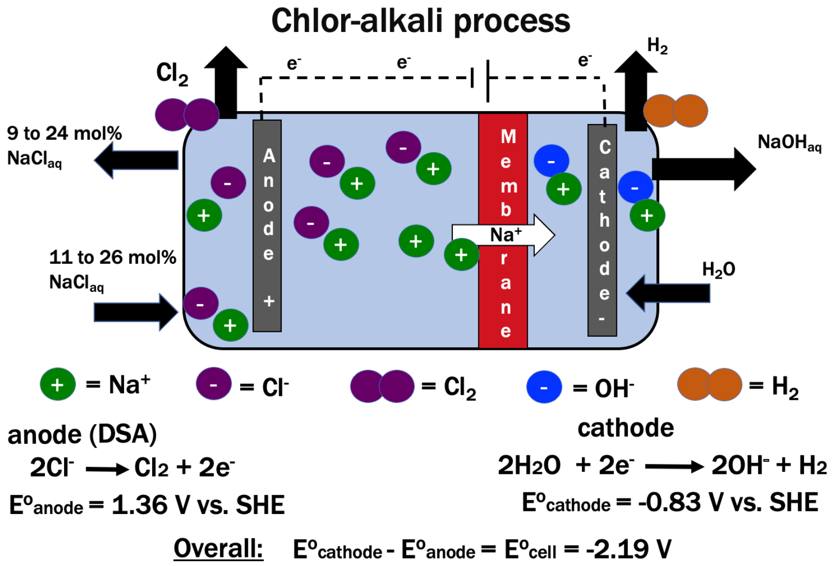

Figure 1. Illustrated chlor-alkali process scheme to produce caustic soda (i.e., sodium hydroxide), hydrogen, and chlorine with half-cell reaction and overall cell voltage for the process.

Most senior design projects utilize a continuous stirred tank reactor (CSTR) or plug flow reactor (PFR) at the heart of their process. The key variables in the design and sizing up these reactors are flow rate, temperature, the selection of the catalyst, and feed concentrations. These inputs, as well as various reactor design equations found in Chemical Reaction Engineering, are used to estimate the volume of the reactor needed (left column of **Table 1**). The number of reactors and their size can influence the CapEx. Once the technical parameters are connected to the cost, the reactor's operating temperature, size, and conversion, are tuned to optimize NPV against given constraints.

At Penn State, the senior design course in previous years asked students to make a first estimate of the reactor volume needed by giving them a rate-law expression and feed concentration. The chlor-alkali process, however, uses an electrolyzer, which is not so much defined by 3-D volume and the cost of a granular catalyst, but is a 2-D area that encompasses the membrane separator and electrodes. Furthermore, traditional rate-law expressions are not used in the sizing up an electrolyzer. The membranes and electrode areas in the electrolyzer dictate the CapEx. The dimensionally stabilized anode (DSA) contains a mixed metal oxide (MMO) of platinum group metals (e.g., iridium and ruthenium oxides) for the chlorine evolution reaction while resisting corrosion.[1] The DSA is the costliest component in a chlor-alkali electrolyzer (> \$5000 m^{-2}). **Table 2** highlights some of the differences between the usual design case encountered in traditional senior design courses in chemical engineering and the chlor-alkali case. **Table 1** compares the design equations used for a CSTR and PFR and a chlor-alkali electrolyzer.

Table 1. Differences in basic design equations for CSTR and PFR and chlor-alkali electrolyzer

Important design equations	
Sizing up CSTR and PFR at steady state CSTR: $r_i = \frac{Q_f}{V_R}\left(C_{i,o} - C_i\right)$ (1) $\tau = \frac{V_R}{Q_f}$ (2) PFR: $r_i = \frac{Q_f}{A_t}\frac{dC_i}{dx}$ (3)[a] [a] constant density fluid & no pressure drop Q_f: fluid volumetric flow rate V_R: reactor volume τ : residence time A_t: Cross-sectional area of the PFR r_i: rate expression for species 'i' C_i: concentration of species 'i' $C_{i,o}$: feed concentration of species 'i'	Sizing up the chlor-alkali electrolyzer at steady state Faraday's Law of electrolysis: $I = nF\frac{dn_i}{dt}$ (4) $A = \frac{I}{i}$ (5) $\frac{dn_i}{dt}$: change in moles of NaOH per time F : Faraday's constant n : # of electrons transferred per OH$^-$ I : change in moles of NaOH per time i : current density for chlor-alkali process (0.4 A cm^{-2}) A : Geometric cell area for the electrolyzer
Energy balances for CSTR and PFRs CSTR: $\dot{Q}_H = \sum_i \Delta H_{Ri} r_i V_R - Q_f \rho_f \hat{C}_P\left(T_f - T\right)$ (6) $\dot{Q}_H = U^o A_h (T_a - T)$ (7) PFR: $\dot{q}_H = \sum_i \Delta H_{Ri} r_i + Q_f \rho_f \hat{C}_P \frac{dT}{dV_R}$ (8)[b] [b] assumes constant pressure and ideal gas $\dot{q}_H = \left(\frac{2}{R}\right) U^o (T_a - T)$ (9) $\dot{Q}_H$: heat input or removal for CSTR $\dot{q}_H$: heat input or removal for PFR R: radius of PFR A_h: area for heat transfer U^o: overall heat transfer coefficient T_a: temperature of the jacket ΔH_{Ri}: heat of reaction ρ_f: density of the fluid $\hat{C}_P$: specific heat capacity of the fluid T_f: feed temperature	Energy considerations for chlor-alkali electrolyzer $\Delta G^o = -nFE^o$ (10) $E_{Nernst} = E^o - \frac{RT}{nF} ln \frac{C_r}{C_o}$ (11) C_r: concentration of reductant; C_o: concentration of oxidant $E(i) = E_{Nernst} + \eta_{act} + \eta_{ohm}$ (12)[c] [c] assume no significant concentration polarization (i.e., no significant mass transfer resistance) η_i: overpotential $\eta_{act} = \frac{RT}{\alpha_{an}F} ln\left(\frac{i}{i_0^{an}}\right) + \frac{RT}{\alpha_{cat}F} ln\left(\frac{i}{i_0^{cat}}\right)$ (13) α_{an} & α_{cath} : transfer coefficients i_0^{an} & i_0^{cat}: exchange current density values $\eta_{ohm} = i \cdot \sum_i R_i = i \cdot \sum_i \frac{d_i}{\kappa_i}$ (14) R_i: ohmic resistance for the membrane, anolyte compartment, or catholyte compartment d_i: thickness of the membrane, anolyte compartment, or catholyte compartment κ_i: ionic conductivity of the membrane, anolyte compartment, or catholyte compartment $Energy\ use = \int (E \cdot I)dt$ (15)

Table 2. Differences between traditional chemical engineering senior process design projects and the chlor-alkali process design

Usual reactor design problem	Chlor-alkali electrolyzer
Design a 3-D volume for a Continuous Stirred Tank Reactor (CSTR) and/or a Plug Flow Reactor (PFR)	Determine the 2-D area for the electrodes and membrane separator
Select a temperature at which to operate the reactor	Select a voltage at which to operate the electrolyzer. The stack can also be operated at an elevated temperature, but it cannot exceed the boiling point of the aqueous feed streams. The internal cell resistances within the stack can be used to elevate the temperature of the stack.
The conversion and reactor size are often governed by reaction rate coefficients that are controlled by the selection of the catalysts	The conversion is governed by cell current density. Increasing the voltage further to drive higher current is only possible to a certain point as one needs to be concerned about component corrosion and other parasitic reactions. The reaction kinetic parameters, which affect the activation overpotential, are normally defined by the exchange current density and Tafel slope. The electrode or electrocatalyst govern the reaction kinetics in the electrolyzer.
The energy use is primarily determined by the amount of heat that needs to be added (if an endothermic reaction) or removed (for an exothermic reaction) to the reactor	Energy use is largely controlled by the cell voltage. The half-cell equilibrium potentials set the floor voltage needed. The floor voltage plus the overpotentials for passage of electrical current dictate the overall cell voltage.
After the reaction, a complex, and often energy intensive, separation process train is used to purify the products	The chlor-alkali electrolyzer features a membrane separator between the anolyte and catholyte compartments leading to separation of NaOH and Cl_2 products. The Cl_2 and the aqueous NaOH solution leaving the electrolyzer stack often needs further drying. The separation and partial purification of products in the chlor-alkali electrolyzer simplifies further downstream separation/purification units (i.e., it is a form of process intensification).

At the onset of the course, Prof. Velegol, the instructor for the senior design course, surveyed the students about their knowledge of electrochemistry. It was assumed that the students would have gotten some exposure to this material in a Physical Chemistry course. However, it is worth noting that several Chemical Engineering curriculums through the United States have removed Physical Chemistry from their required courses to accommodate other courses such as process safety, statistics, etc.. The survey revealed that the students had little memory of electrochemistry concepts. Prof. Velegol asked Prof. Arges, an electrochemical engineer, to give a one-day lecture on electrochemical engineering principles and its relation to a chloro-alkali process. In the lecture, Prof. Arges covered concepts such as half reactions, Faraday's Law of electrolysis, electrochemical thermodynamics, and sources of overpotential. He did not provide extensive detail about concepts like the Butler-Volmer equation and the Nernst-Planck framework for predicting ionic conductivity; rather, he simply presented a graph of reaction rate (mol/m^2-sec), expressed as current density (A/cm^2), versus cell voltage (i.e., a polarization curve). He showed the students that the cell voltage arises from the standard thermodynamic potentials for the reaction and the departure from the cell voltage occurs via various overpotentials related to reaction kinetics (i.e., activation overpotential – which can be determined using the Butler-Volmer equation), ohmic losses (e.g., ion transport in the aqueous electrolytes and across the membrane separator), and mass transfer (i.e., concentration overpotential). Prof. Arges demonstrated that the current density reflects the production rate of the product depending on the Faradaic efficiency (i.e., the electrical current utilized to make the desired product at an electrode).

Another topic cover in this one-day lecture was the tradeoff between OpEx and CapEx in the chlor-alkali process (**Fig. 2**). The size of the electrolyzer, namely membrane and electrode area, and the CapEx were reduced by increasing the cell voltage (i.e., applying more overpotential) so a higher current density can be attained. Of course, this increased the OpEx through wasted electrical energy. Prof. Arges also discussed how materials innovation, such as reducing ohmic overpotentials via more conductive membrane separators, can reduce the electrolyzer size and CapEx without necessarily increasing the OpEx. Reducing the various overpotentials through materials innovation enable the process to run at a higher current density for a given voltage when benchmarked against a system without membrane and electrode improvements. It is worth mentioning that chemical engineering process design courses normally use Aspen Plus to design the reactors and the overall process. However, Aspen Plus does not have standard electrolyzer modules and the use of a process design software package proved to be too difficult in the end for this one semester course. Prof. Velegol thought it was an advantage for the students to perform their own calculations and to think about the design equations rather than using a simulation software package.

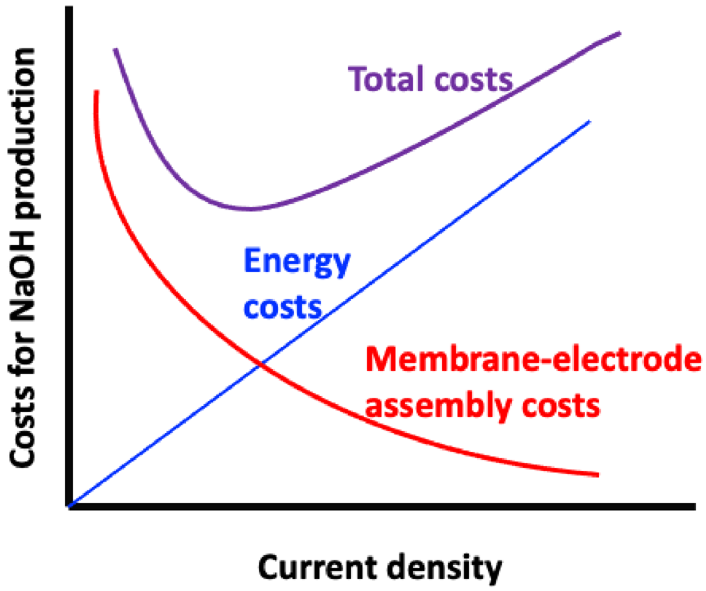

Figure 2. OpEx, CapEx, and total costs for a chlor-alkali electrolysis process

The final part of the one-day lecture covered alternative process designs for caustic soda production and a brief discussion of different membrane separators for the chlor-alkali process. The chlor-alkali process is recognized for being energy intensive. Its large energy use arises from the minimum cell voltage needed (-2.2 V) for the chlorine evolution reaction and the water reduction reaction. Because there are regions across the globe where electricity costs are not low, an alternative chlor-alkali process has been developed using an oxygen depolarized cathode (ODC). The ODC chlor-alkali process (**Fig. 3a**) performs oxygen reduction at the cathode under basic conditions. This reduces the minimum cell voltage by 1.23 V (-0.96 V versus -2.19 V). ODC chlor-alkali, however, does not generate hydrogen as a by-product. For most industrial applications that only desire caustic soda or chlorine, the absence of hydrogen product is satisfactory as the other plant operations in close vicinity do not have a need for the hydrogen product (i.e., a sizeable amount of the hydrogen is often vented).[2] Another process design for caustic soda production involves bipolar membrane (BPM) electrodialysis (ED) (**Fig. 3b**). This process generates a sodium hydroxide stream and a hydrochloric acid stream from aqueous sodium chloride feed streams. Lienhard and co-workers recently reported that BPMED offers the lowest specific energy use for sodium hydroxide from a theoretical analysis when compared to conventional chlor-alkali.[3] The process does not perform chlorine evolution reaction. However, BPMED in practice shows comparable or slightly higher energy use when compared to chlor-alkali. The authors assert that further research is needed in BPMED to improve its energy efficiency. More recently, Arges et al. demonstrated BPM membrane capacitive deionization (BPM MCDI) to make an alkaline process stream (i.e., aqueous sodium hydroxide) from aqueous saline feed.[4] BPM MCDI does not generate hydrogen or oxygen gas and it uses low-cost carbon cloth electrodes.

Chlor-alkali processes have historically featured three types of cell designs: i) mercury flow cell, ii) diaphragm membrane, and iii) a cation exchange membrane. The mercury flow has been phased out due to environmental concerns.[1] The cation exchange membrane separator, which uses one layer of perfluorosulfonic acid and another layer of perfluorocarboxylic acid, is the preferred membrane separator today as the diaphragm membrane contains asbestos. The perfluorocarboxylic acid layer in the cation exchange membrane mitigates hydroxide ion crossover from the catholyte compartment to the anolyte compartment. This is important for preventing corrosion of the DSA. The cation exchange membrane chlor-alkali process operates at a lower cell voltage and higher current density as it has a lower ohmic overpotential. This leads to the cation exchange membrane chlor-alkali process having a lower specific energy consumption for sodium hydroxide. However, perfluorinated cation exchange membranes are quite costly (~\$500 m^{-2}) when compared to diaphragm separators. This is an additional example showing the trade-off between CapEx and OpEx.

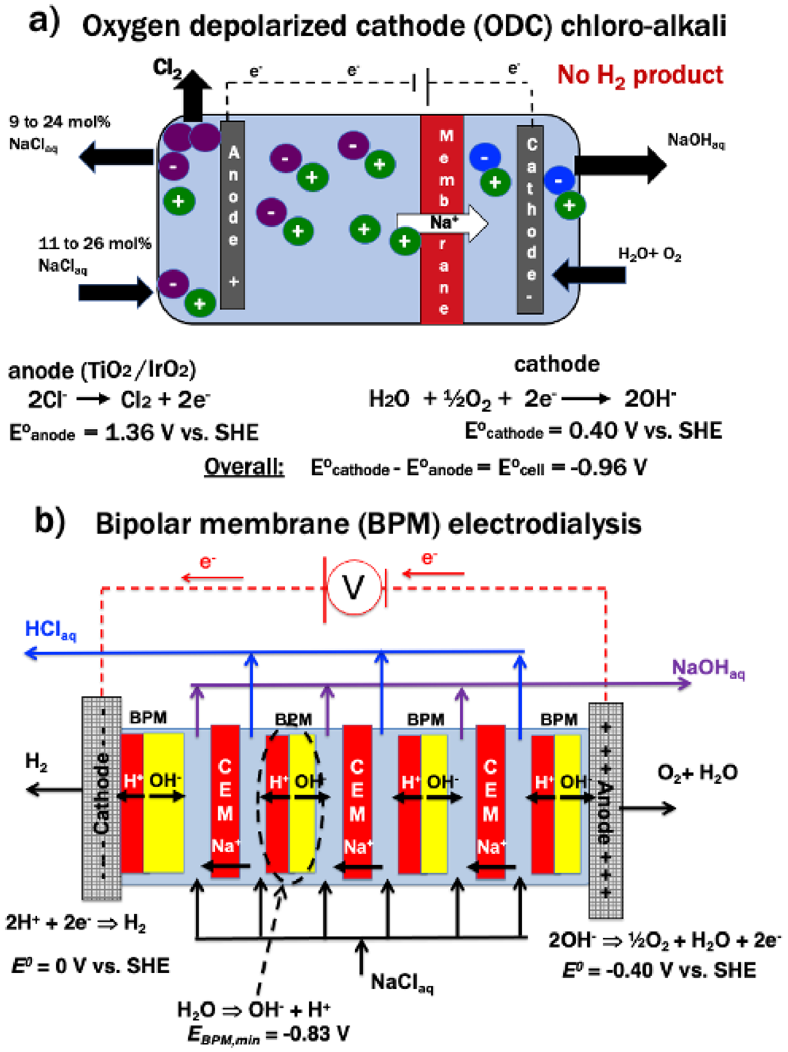

Figure 3. Alternative processes for caustic soda production: a) ODC chlor-alkali and b) BPMED.

In short, the traditional Chemical Engineering Senior Process Design course is an effective place for students to learn electrochemical engineering concepts and to design chemical processes that are powered on renewable electrons. At the end of the course, Prof. Velegol observed that the students were effective in applying the equations to make calculations about the size, energy use, and cost of the chlor-alkali electrolyzer. This senior design project can be improved by having students come into the course with a stronger foundation in electrochemical engineering. This potentially could be accomplished by introducing the core principles of electrochemical engineering in the core chemical engineering courses (e.g., thermodynamics, transport phenomena, and reaction engineering) before process design – as discussed in last year's E-Chem Education article.[5] Overall, we envision that the chlor-alkali process design course can be adopted by other instructors teaching senior process design. There is ample opportunity to modify the course objectives by comparing processes with different membrane separators or different unit operations (e.g., BPMED versus ODC chlor-alkali).

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