NAWI National Alliance
for Water Innovation

Assessing Electrodialysis Systems for Concentrating High-Salinity Brines

Hunter Barber

West Virginia University

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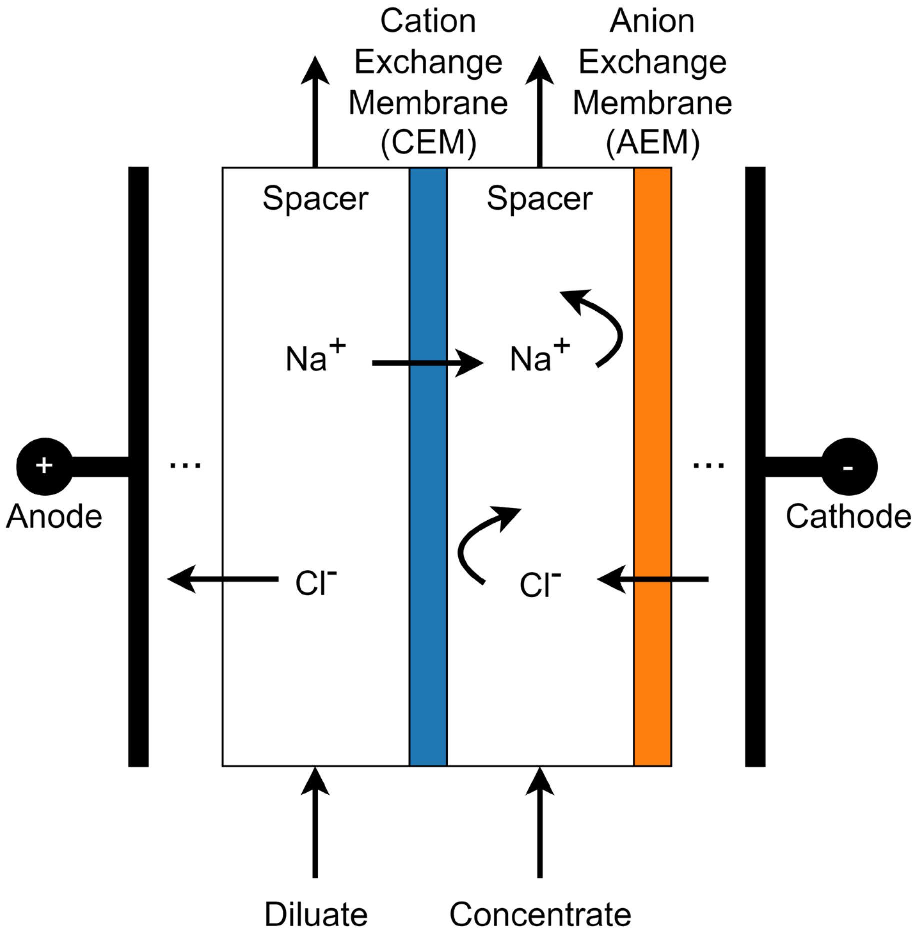
Background on Electrodialysis Technologies for Desalination

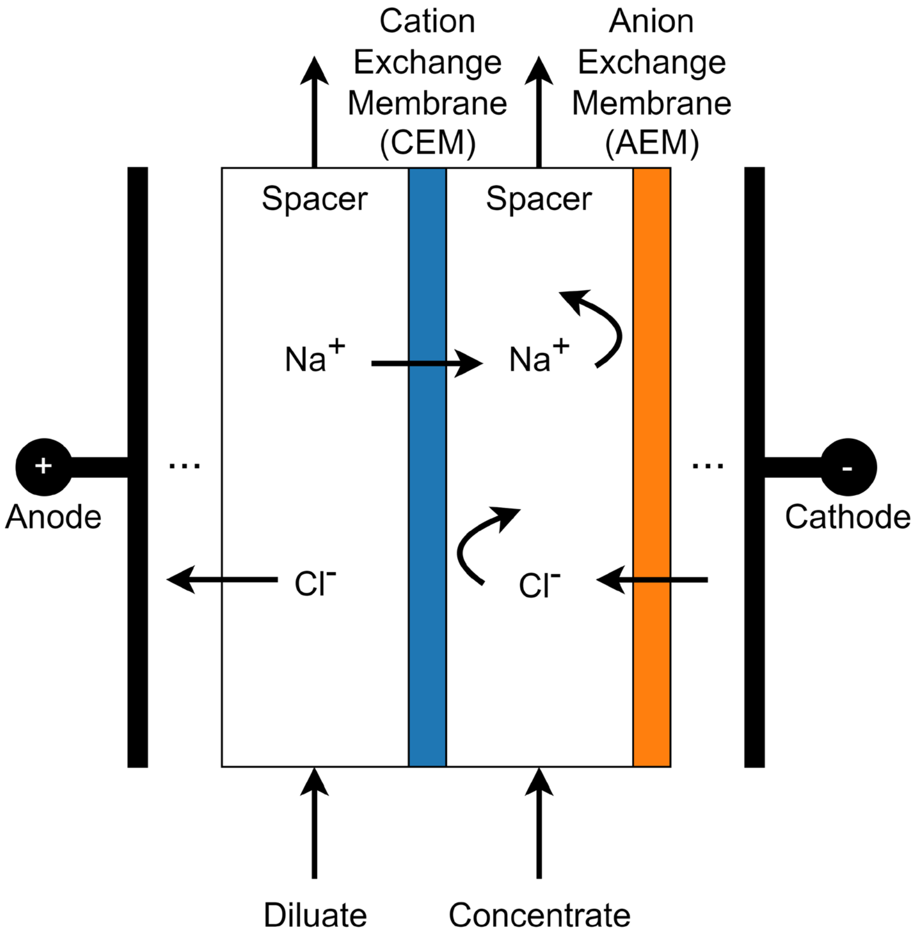
- Electrodialysis (ED) is an electrically-driven membrane-based desalination technology
    - Electrified process capable of integrating with renewable energy sources
    - Industry application is generating a purified diluate from low-salinity feedwaters
- Specialized electrodialysis configurations and operation
    - Selective electrodialysis (SED)
    - Reverse electrodialysis (RED)
    - **Electrodialysis of high-salinity brines[1,2]**



[1] Chehayeb, et al. 2017. *Desalination*.
[2] McGovern, et al. 2014. *Appl. Energy*.

Objective of Assessing Electrodialysis Brine Concentrator Systems

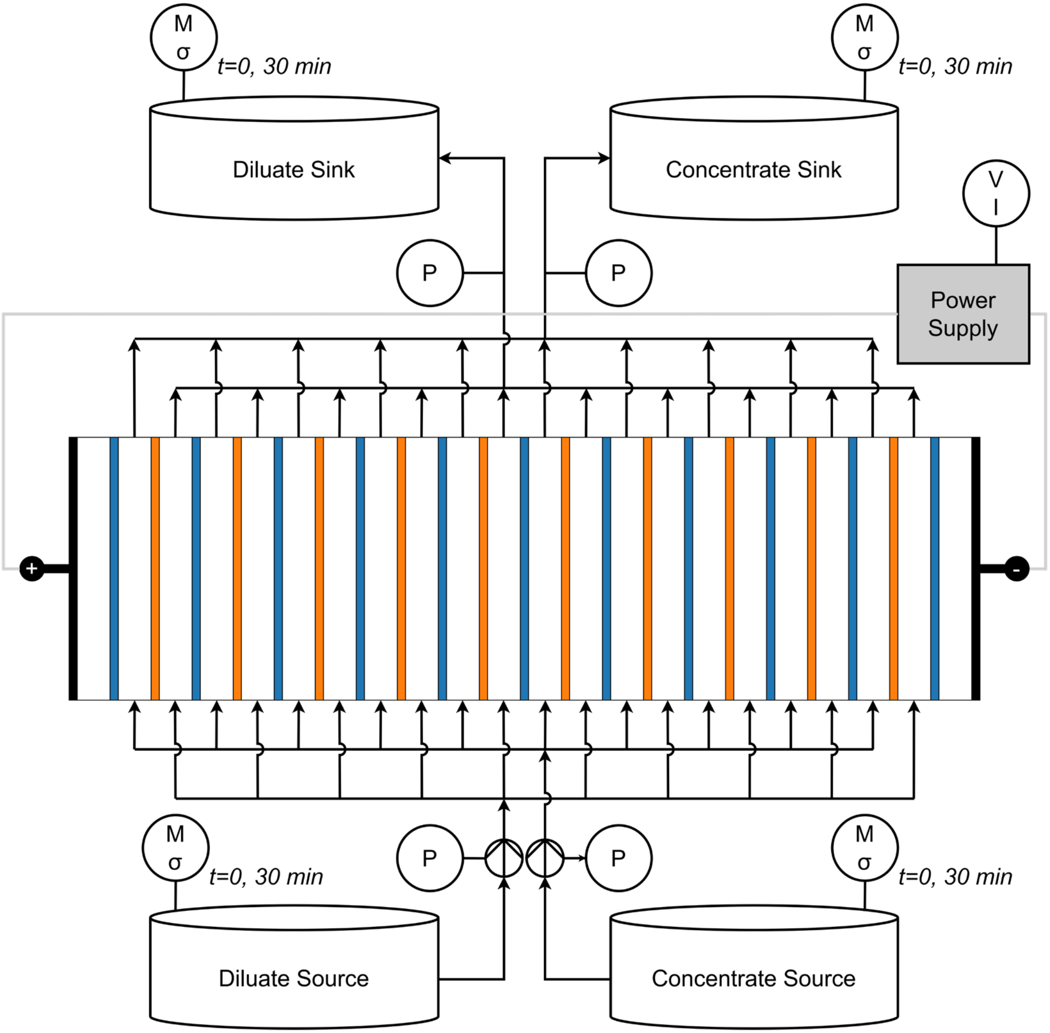
- Electrodialysis brine concentrator (EDBC) systems are for brine production requiring high-salinity operation
    - Process goal changes to producing a high-salinity brine concentrate
- **Objective is to use WaterTAP for a model-based technoeconomic analysis and optimization of an industrial-scale EDBC**
    - Model validation with experimental data
    - Process optimization
- EDBC analysis is a collaboration with New Mexico State University experimental group[3]



[3] Xu, et al. 2021. *Membranes*.

Understanding the Information Available from EDBC Experiments

- Instrumental measurements from lab-scale EDBC experiments
    - Geometry of ED components
    - Inlet and outlet states defined by **total mass (M)** and **conductivity (σ)** before and after 30 minutes of steady-state operation
    - **Pressure (P)** at the inlet and outlet of the diluate and concentrate
    - **Current (I)** and **voltage (V)** measured over the entire stack
- Measurements suitable for model validation
    - Current density (constant voltage)
    - Net salt permeation
    - Net water permeation



Understanding the Information Available from EDBC Experiments

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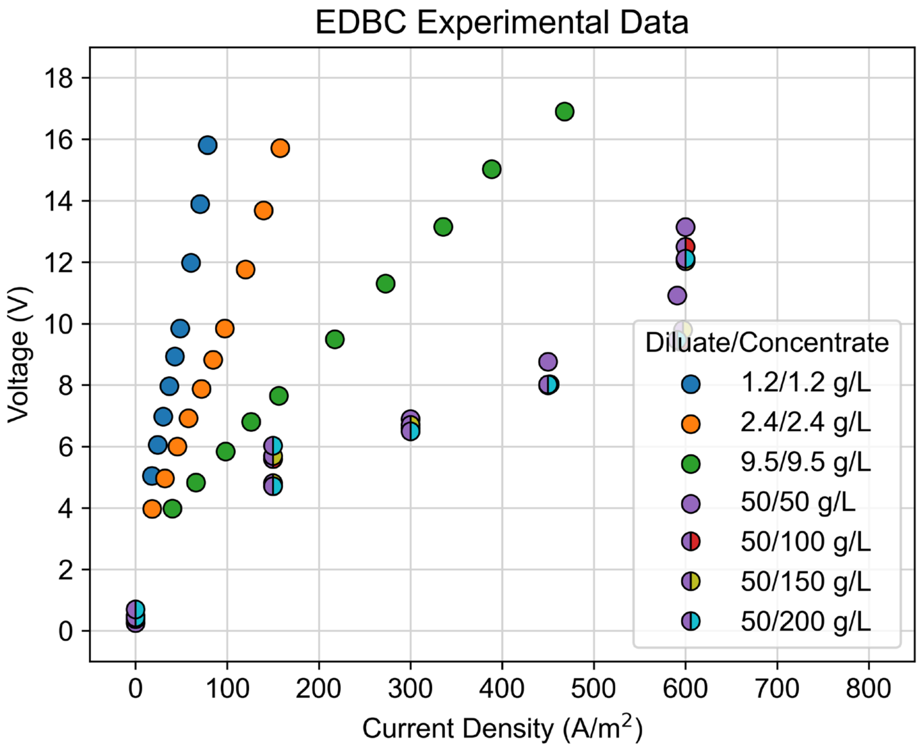
    - **Pressure (P)** at the inlet and outlet of the diluate and concentrate
    - **Current (I)** and **voltage (V)** measured over the entire stack
- Operating conditions
    - Variable concentration (up to 200 g/L) and concentration gradient
    - Incremental operating current/voltage

The information that can be interpreted from experiments directly affects how the model can be parameterized and validated



How Does Experimental Measurement Availability Affect the EDBC Model Parameterization?

u	Voltage	ξ	Current utilization	x	Position in length domain
i	Current density	F	Faraday's constant	$ohm, nonohm$	Ohmic, Nonohmic
r	Areal resistance	D	Diffusion coefficient		Ion, anion, cation exchange membrane
ϕ	Potential loss				ffusion layer
h	Height				ft, right relative position
Δ	Diffusion layer thickness				luate, Concentrate
κ	Equivalent conductivity				lectrode
n_{cp}	Number of cell pairs	MW	Molecular weight	tot	Total
J	Flux	t	Transport number	z	Charge

14 fixed model parameters dependent on the system design, operation and material properties need to be regressed

Electrochemical Performance

$$u(x) = i(x) r_{tot}(x) + \phi_{dl}^{ohm}(x) + \phi_{dl}^{nonohm}(x)$$

$$r_{tot}(x) = n_{cp}\left(\boxed{r^{cem}} + \boxed{r^{aem}} + \frac{h^{spacer} - \Delta^{L,cem}(x) - \Delta^{R,aem}(x)}{\kappa^{con}(x)} + \frac{h^{spacer} - \Delta^{R,cem}(x) - \Delta^{L,aem}(x)}{\kappa^{dil}(x)}\right) + \boxed{r_{el}}$$

Mass Transport

$$J_j^{con}(x) = -J_j^{dil}(x) = \left(\boxed{t_j^{cem}} - \boxed{t_j^{aem}}\right)\frac{\boxed{\xi} i(x)}{z_j F} - \left(\frac{\boxed{D_j^{cem}}}{h^{cem}}\left(C_j^{L,cem}(x) - C_j^{R,cem}(x)\right) + \frac{\boxed{D_j^{aem}}}{h^{aem}}\left(C_j^{R,aem}(x) - C_j^{L,aem}(x)\right)\right);\ j \in Na^+, Cl^-$$

$$J_w^{con}(x) = -J_w^{dil}(x) = \left(\boxed{t_w^{cem}} + \boxed{t_w^{aem}}\right)\frac{i(x)}{F} + \left(\boxed{L^{cem}}\left(\pi^{L,cem}(x) - \pi^{R,cem}(x)\right) + \boxed{L^{aem}}\left(\pi^{R,aem}(x) - \pi^{L,aem}(x)\right)\right)$$

How Does Experimental Measurement Availability Affect the EDBC Model Parameterization?

Parameters that are indistinguishable based on experimental information available

- The properties and transport of the CEM and AEM
- The contribution of the electrode and membrane resistances in series
- The contribution of transport number and current utilization on salt transport

Fundamental ED modeling assumptions

- Assert electroneutrality throughout the stack

Literature-based model functions to capture experimental trends

- Nonohmic potential losses are a function of current density[4]
- Resistance is a function of concentration[5]

$$\boxed{\phi_{eop}(x)} = \frac{RT}{\alpha F} ln\left(\frac{i(x)}{i_o}\right) \qquad \boxed{r^{iem}(x)} = A + \frac{B}{C_{NaCl}^{dil}(x)}$$

Electrochemical Performance

$$u(x) = i(x) r_{tot}(x) + \phi_{dl}^{ohm}(x) + \phi_{dl}^{nonohm}(x) \boxed{+ \phi_{equ} + \phi_{eop}(x)}$$

$$r_{tot}(x) = n_{cp}\left(\boxed{r^{cem} + r^{aem}} + \frac{h^{spacer} - \Delta^{L,cem}(x) - \Delta^{R,aem}(x)}{\kappa^{con}(x)} + \frac{h^{spacer} - \Delta^{R,cem}(x) - \Delta^{L,aem}(x)}{\kappa^{dil}(x)}\right) + \boxed{\cancelto{0.01\ A/m^2}{r_{el}}}$$

Mass Transport

$$J_j^{con}(x) = -J_j^{dil}(x) = \left(\boxed{\cancelto{0.95}{t_j^{cem}} - t_j^{aem}}\right)\frac{\boxed{\xi} i(x)}{z_j F} - \left(\frac{\boxed{D_j^{cem}}}{h^{cem}}\left(C_j^{L,cem}(x) - C_j^{R,cem}(x)\right) + \frac{\boxed{D_j^{aem}}}{h^{aem}}\left(C_j^{R,aem}(x) - C_j^{L,aem}(x)\right)\right);\ j \in \boxed{Na^+, Cl^-}$$

$$J_w^{con}(x) = -J_w^{dil}(x) = \left(\boxed{t_w^{cem} + t_w^{aem}}\right)\frac{i(x)}{F} + \left(\boxed{L^{cem}}\left(\pi^{L,cem}(x) - \pi^{R,cem}(x)\right) + \boxed{L^{aem}}\left(\pi^{R,aem}(x) - \pi^{L,aem}(x)\right)\right)$$

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- The properties and transport of the CEM and AEM
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  resistances in series
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Fundamental ED modeling assumptions

- Assert electroneutrality throughout the stack

Literature-based model functions to capture

- s are a function of current
  density
- Resistance is a function of concentration[5]

9 fixed model parameters dependent on the system design, operation and material properties need to be regressed

$$\phi_{eop}(x) = \frac{RT}{\boxed{\alpha} F} ln\left(\frac{i(x)}{\boxed{i_o}}\right) \qquad r^{iem}(x) = \boxed{A} + \frac{\boxed{B}}{C^{dil}_{NaCl}(x)}$$

Electrochemical Performance

$$u(x) = i(x) r_{tot}(x) + \phi^{ohm}_{dl}(x) + \phi^{nonohm}_{dl}(x) + \boxed{\phi_{equ}} + \phi_{eop}(x)$$

$$r_{tot}(x) = n_{cp}\left(r^{iem}(x) + \frac{h^{spacer} - \Delta^{L,cem}(x) - \Delta^{R,aem}(x)}{\kappa^{con}(x)} + \frac{h^{spacer} - \Delta^{R,cem}(x) - \Delta^{L,aem}(x)}{\kappa^{dil}(x)}\right) + r_{el}$$

Mass Transport

$$J^{con}_j(x) = -J^{dil}_j(x) = (2t^{cem}_{co} - 1)\frac{\boxed{\xi} i(x)}{z_j F} - \boxed{D^{iem}_j}\left(\frac{1}{h^{cem}}\left(C^{L,cem}_j(x) - C^{R,cem}_j(x)\right) + \frac{1}{h^{aem}}\left(C^{R,aem}_j(x) - C^{L,aem}_j(x)\right)\right);\ j \in NaCl$$

$$J^{con}_w(x) = -J^{dil}_w(x) = \boxed{t^{iem}_w}\frac{i(x)}{F} + \boxed{L^{iem}}\left(\left(\pi^{L,cem}(x) - \pi^{R,cem}(x)\right) + \left(\pi^{R,aem}(x) - \pi^{L,aem}(x)\right)\right)$$

Formulating the Parameter Regression for the EDBC Model

- Simulate the model at experimental conditions for validation
- Utilize **single objective functions** to isolate parameters in performance subproblems
    - Different error functions selected based on validation variable
        - Relative Sum of Squared Errors (RSSE)
        - Scaled Sum of Squared Errors (SSSE)
    - Newton-Raphson method performed to converge on optimal parameter values

Iteration	$RSSE_{el}$	$SSSE_{NaCl}$	$SSSE_w$
0	-	-	-
1	5.48×10^{-1}	1.91×10^{-4}	3.01×10^{-3}
2	5.48×10^{-1}	1.68×10^{-4}	2.65×10^{-3}

$$\min_{x_{el}} \quad RSSE_{el} = \sum_{j=0}^{n} \frac{\left(i_n - \frac{\sum_{x=0}^{k} \hat{\imath}_n(x)}{k}\right)^2}{\left(\frac{\sum_{x=0}^{k} \hat{\imath}_n(x)}{k}\right)}$$

$$if\ V_n^{app} > 0$$

$$x_{el} = \{\phi_{equ}, \alpha, i_o, A, B\}$$

$$\min_{x_{NaCl}} \quad SSSE_{NaCl} = \sum_{k=0}^{n} \left(1\times10^{6}\left(\dot{m}_{NaCl,n}^{perm} - \widehat{\dot{m}}_{NaCl,n}^{perm}\right)\right)^2$$

$$if\ E_n < 1\times10^{-4}$$

$$x_{NaCl} = \{\xi, D_{NaCl}^{iem}\}$$

$$\min_{x_w} \quad SSSE_w = \sum_{k=0}^{n} \left(1\times10^{6}\left(\dot{m}_{w,n}^{perm} - \widehat{\dot{m}}_{w,n}^{perm}\right)\right)^2$$

$$if\ E_n < 1\times10^{-4}$$

$$x_w = \{t_w^{iem}, L^{iem}\}$$

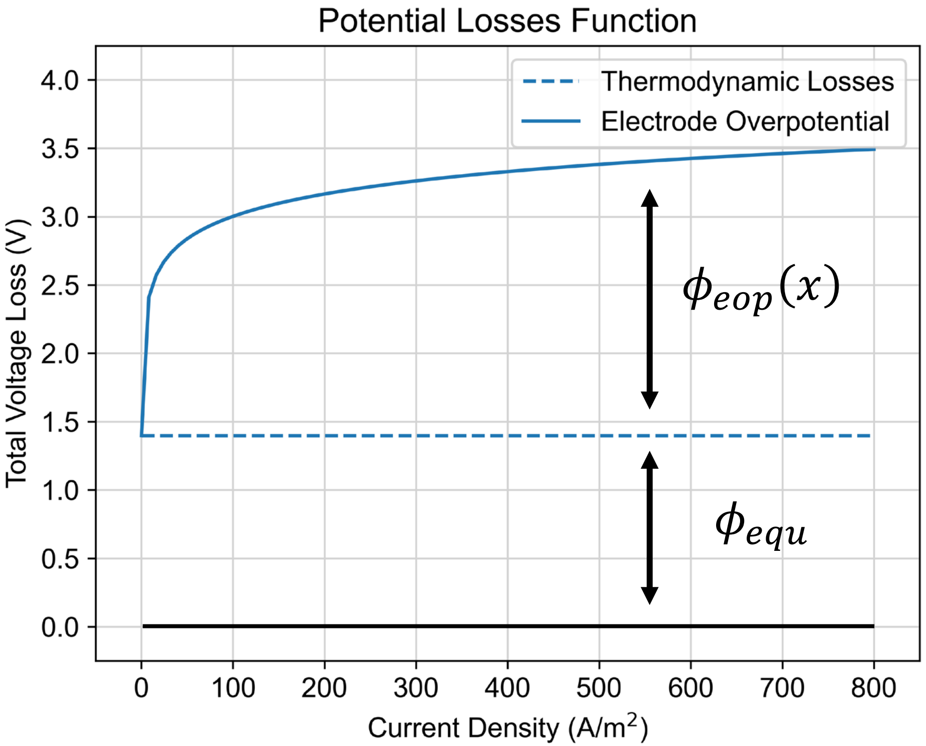
Validating the Parameterized EDBC Model with Experimental Data

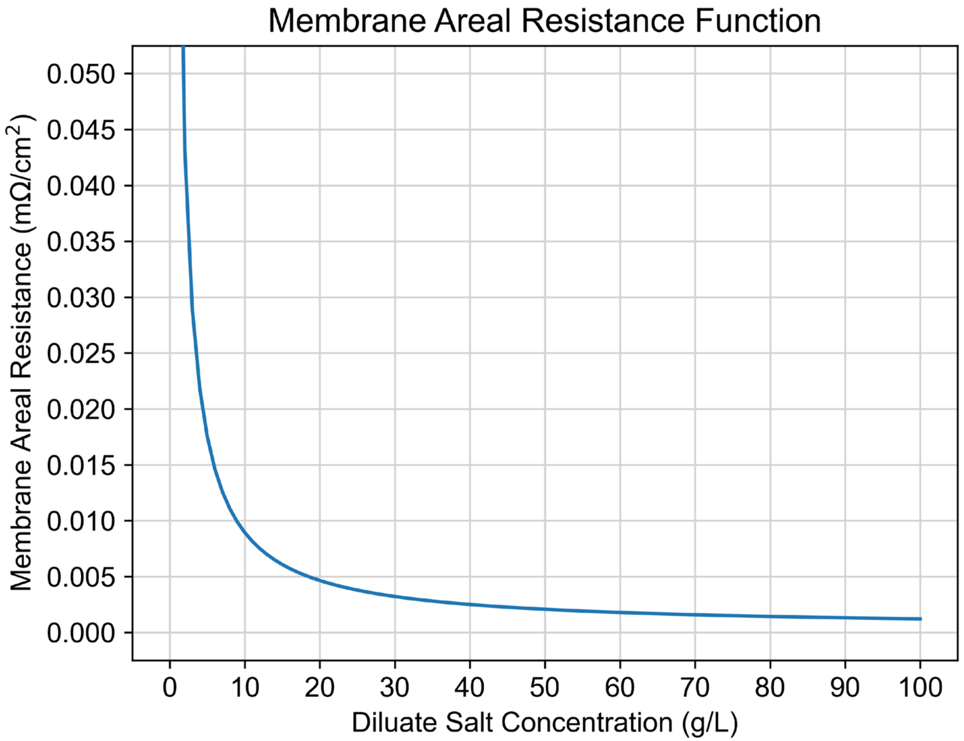
Electrochemical Performance

- Added electrochemical model functions

$$\phi_{equ}, \qquad \phi_{eop}(x) = \frac{RT}{\alpha F} ln\left(\frac{i(x)}{i_o}\right)$$

$$r^{iem}(x) = A + \frac{B}{C_{NaCl}^{dil}(x)}$$



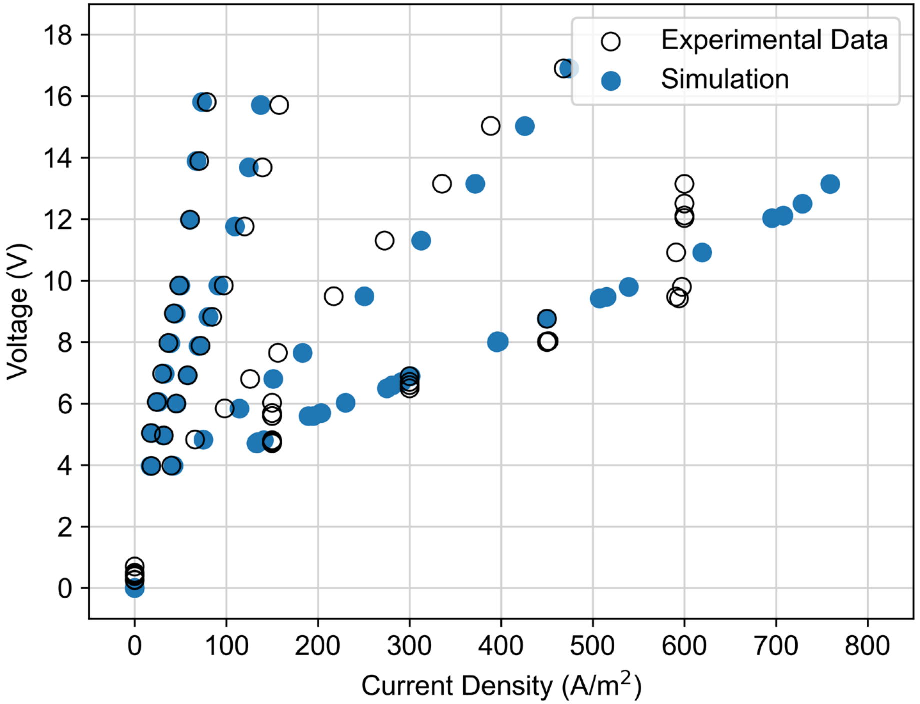


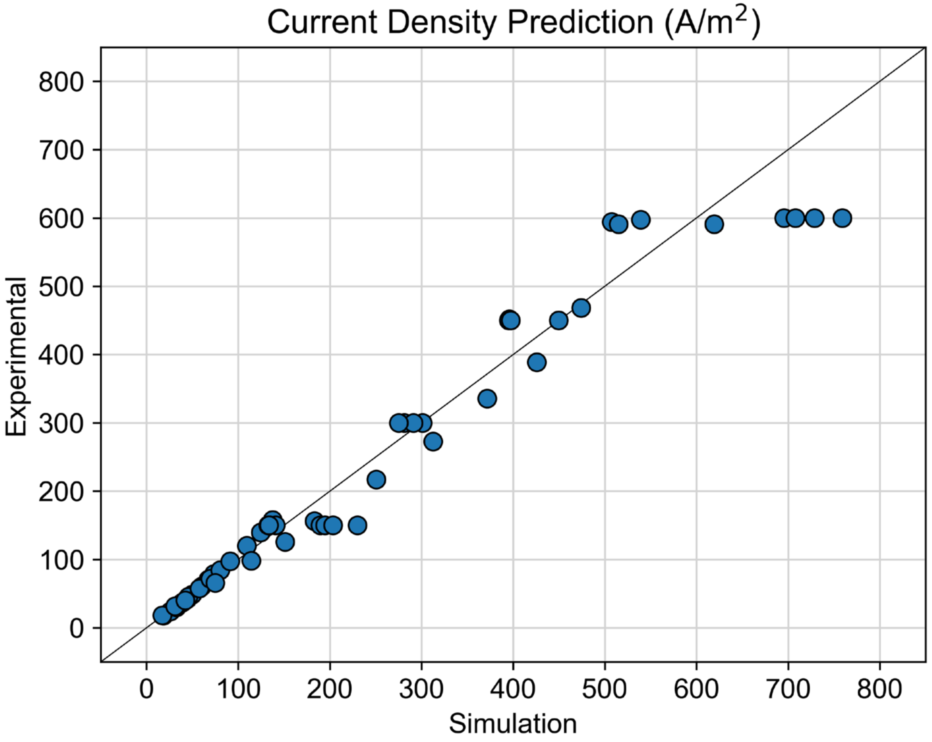
[4] Walker, et al. 2014. *Desalination*.
[5] Galama et al. 2014, *J. Mem. Sci.*

Validating the Parameterized EDBC Model with Experimental Data

Electrochemical Performance

- Some mismatch attributed to comparing constant voltage/current density experimental measurements with average voltage/current 1D model predictions

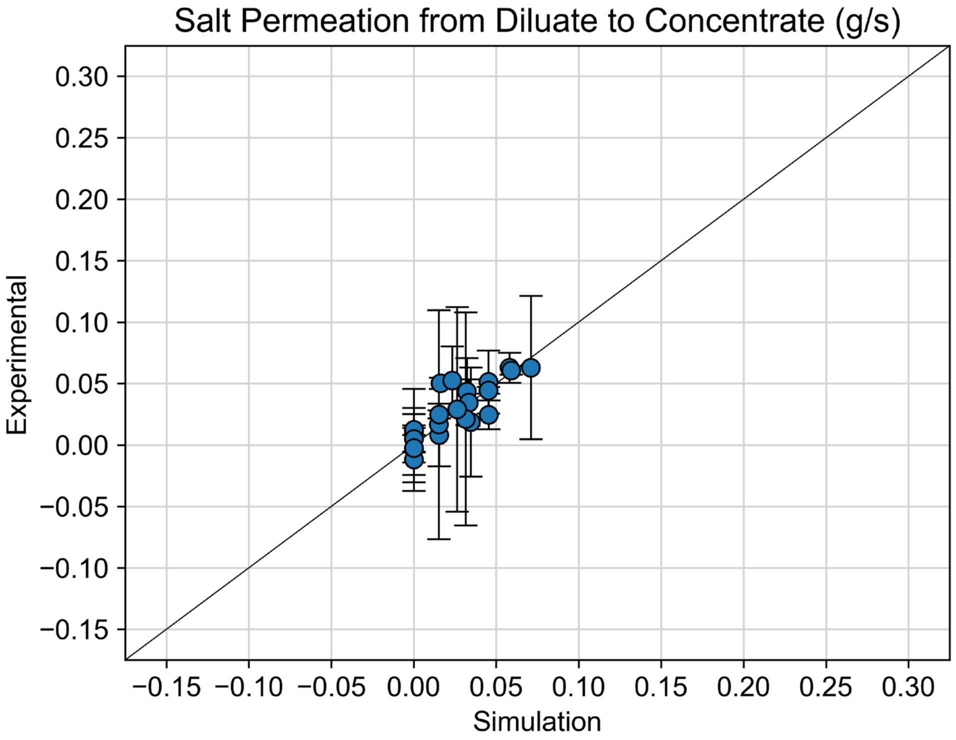


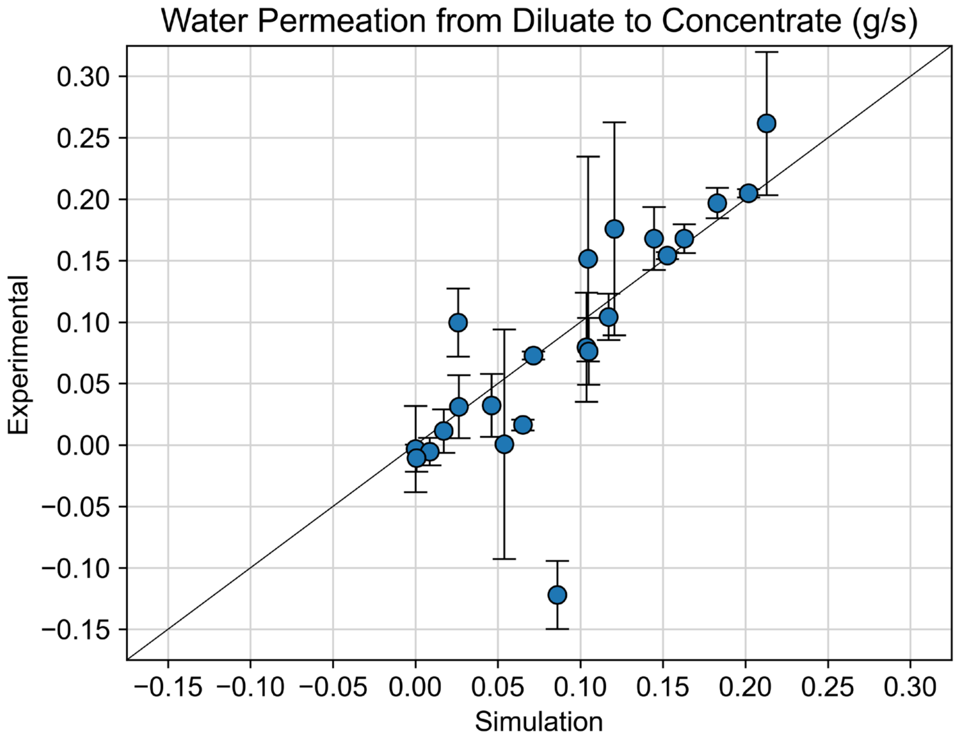


Validating the Parameterized EDBC Model with Experimental Data

Mass Transport

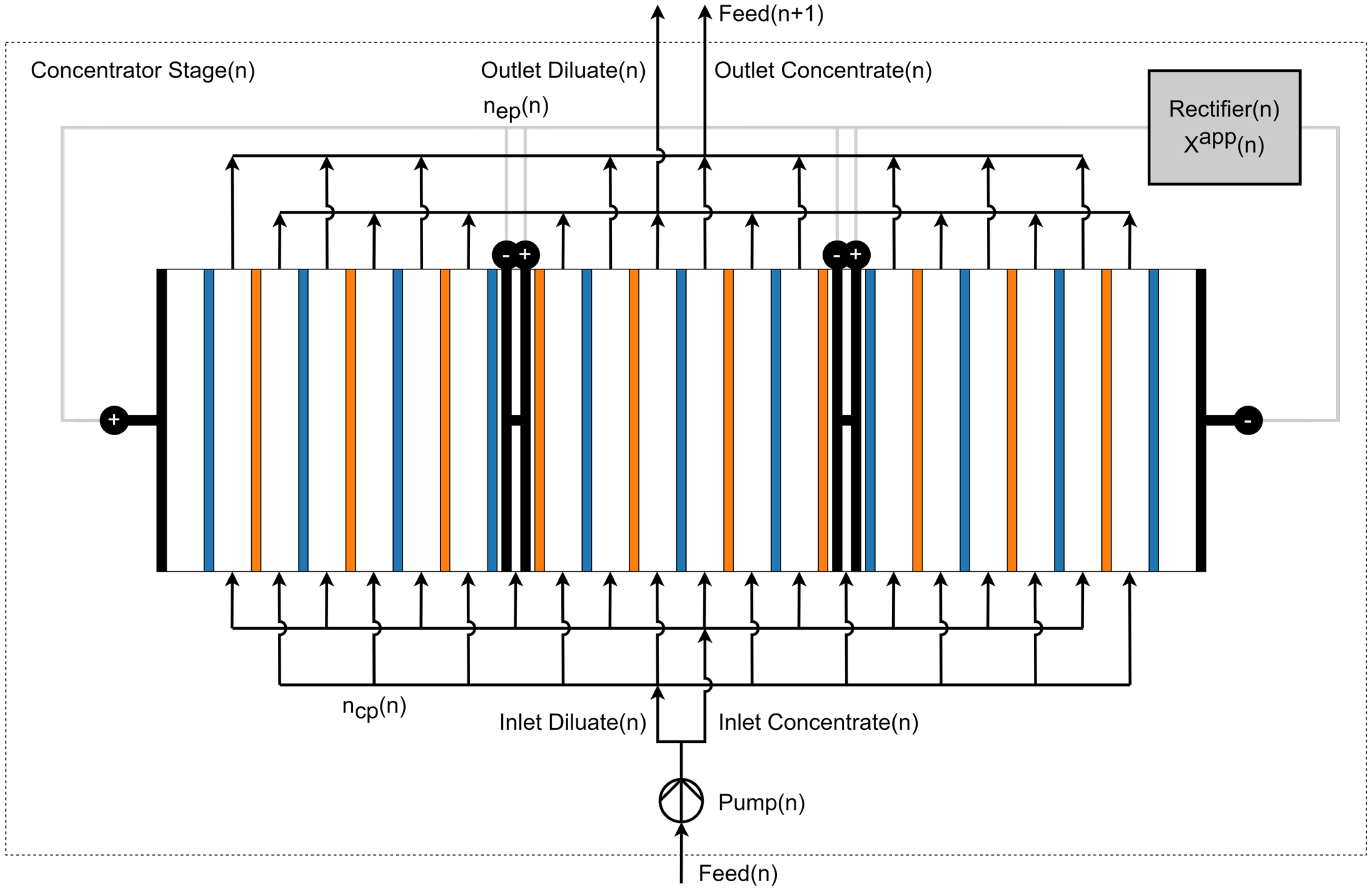
- Error bars show overall mass balance error in experimental data





Simulating and Optimizing the EDBC Model at the Industrial-Scale

- EDBC system for industry operation
    - Bench-scale concentrated brine by **14%** at a **1 LPM** capacity
    - Industrial-scale assumed to concentrate brine from **5 to 20 wt% (a 340% increase)** at a **0.1 MGD (263 LPM)** capacity
- Generalize an *n*-stage flowsheet simulation for optimization
    - Multiple stages necessary for higher-degree of concentration
    - Any *n*-stage EDBC system can be simulated provided a preselected argument



Formulating the EDBC System Optimization

- **Objective function** formulated as cost-effective production of high-salinity brine
- Number of cell pairs (n_{cp}) and electrical stages (n_{ep}) modeled as **continuous decision variables**
- Operation bounded below 1000 A/m^2 to avoid (unmodeled) energy loss as heat
- **Features imposed for design and manufacturing practicality**
  - Length and width of ED components optimized across all stages for modularity
  - Economies of scale introduced by 6/10^{ths} rule for modular ED components[6]

$$\min_{x} \quad LCOB = \frac{f_{crf} C_{cap} + C_{op}}{f_{util} \dot{m}_{NaCl}^{out}}$$

$$x = \{L, w, n_{cp}(n), n_{ep}(n), X^{app}(n)\}$$

$$where \quad n = \{1, 2, 3, \ldots\} \equiv concentrator\ stages$$

$$X^{app} = \{V^{app}, I^{app}\} \equiv constant\ operation\ mode$$

$$s.t. \quad process\ model\ flowsheet$$

$$x_{NaCl}^{product} \geq 0.20$$

$$L = L(n)$$

$$w = w(n)$$

$$f_{EOS} = \frac{A_{ref}}{A}\left(\frac{A}{A_{ref}}\right)^{0.6}, \quad A_{ref} = 0.5\ m^2$$

$$C_{cap}^{ED(n)} = f_{TIC}\left(2 f_{EOS} C_{unit}^{iem} A n_{cp} + 2 f_{EOS} C_{unit}^{el} A n_{ep} + C_{cap}^{rect}\right)$$

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[6] Turton, et al. 2017. *Prentice Hall*.

EDBC System Optimization Results and Conclusions

- Exhaustively simulate constant operation mode and number of concentrator stages decisions
  - 4 or less concentrator stages cannot achieve 20 wt% brine quality
  - More stages progressively increase costs

Concentrator stages	**-**	5	6	5	6
Constant operation mode	**-**	Voltage	Voltage	Current	Current
Brine quality, $x_{NaCl}^{product}$	**-**	0.215	0.232	0.212	0.230
Brine recovery	**-**	0.174	0.171	0.163	0.153
LCOB	**\$/kg**	0.0520	0.0616	0.0516	0.0623
SECB	**kWh/kg**	0.116	0.131	0.126	0.147
LCOW	**\$/m^3**	13.8	17.7	13.5	17.7
SECW	**kWh/m^3**	24.9	30.4	26.8	33.8
Cell length, L	**m**	6.84	6.91	6.80	5.98
Cell width, w	**m**	0.157	0.155	0.105	0.123

EDBC System Optimization Results and Conclusions

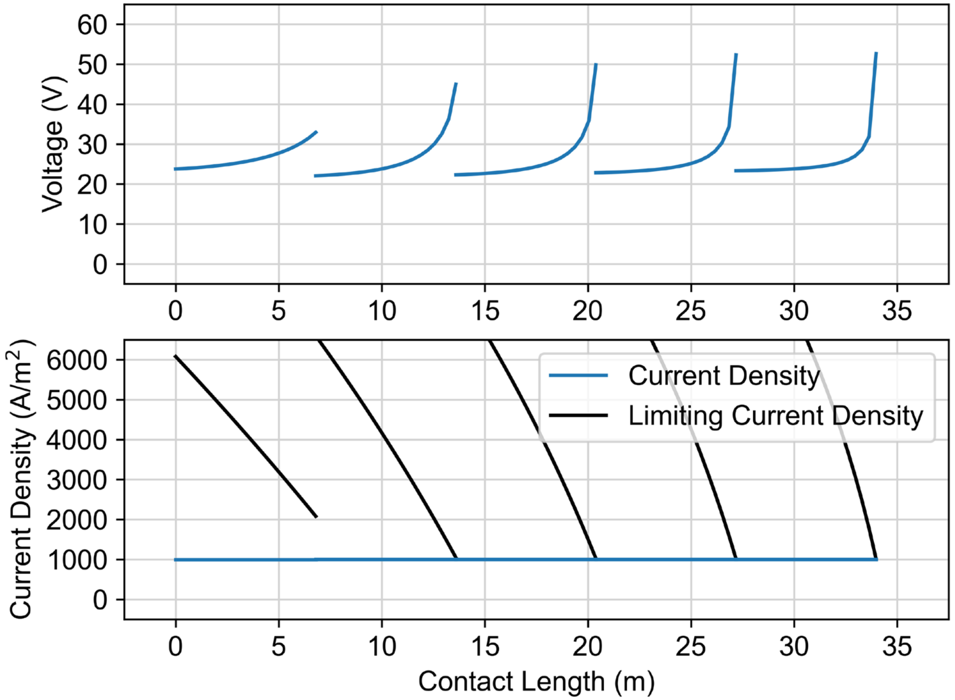
- Review optimal decision variables across each concentrator stage of the EDBC system

Concentrator stages	**-**	5
Constant operation mode	**-**	Current
Brine quality, $x_{NaCl}^{product}$	**-**	0.212
Brine recovery	**-**	0.163
LCOB	**\$/kg**	0.0516
SECB	**kWh/kg**	0.126
LCOW	**\$/m^3**	13.5
SECW	**kWh/m^3**	26.8
Cell length, L	**m**	6.80
Cell width, w	**m**	0.105

	Number cell pairs	**Number electrode pairs**	**Operating current density**	**Outlet con. flow**	**Outlet con. mass fraction**
	-	**-**	**A/m^2**	**MGD**	**-**
0	-	-	-	0.0500	0.050
1	316	8	1000	0.0568	0.074
2	335	8	1000	0.0356	0.109
3	325	6	1000	0.0248	0.149
4	317	4	1000	0.0192	0.185
5	312	4	1000	0.0163	0.212

EDBC System Optimization Results and Conclusions

- Review optimal decision variables across each concentrator stage of the EDBC system
  - Operating current density bounded but approaches limiting current density, $i_{lim}(x) = f\big(C(x), v(x)\big)$



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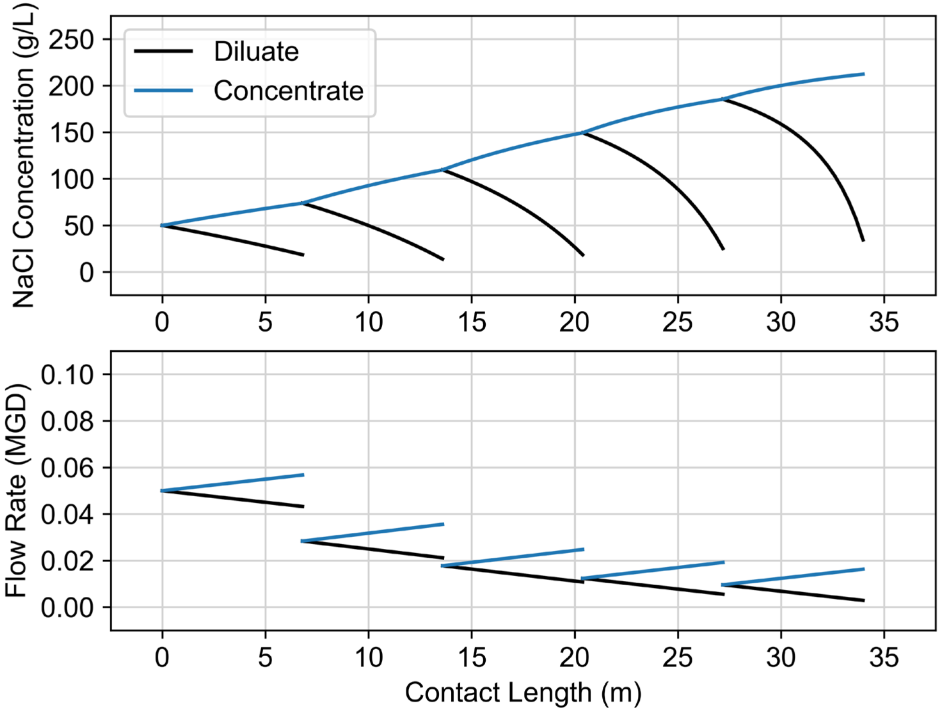
EDBC System Optimization Results and Conclusions

- Review optimal decision variables across each concentrator stage of the EDBC system
  - Operating current density bounded but approaches limiting current density, $i_{lim}(x) = f\big(C(x), v(x)\big)$
  - Concentrate state profile along simulated 1D length



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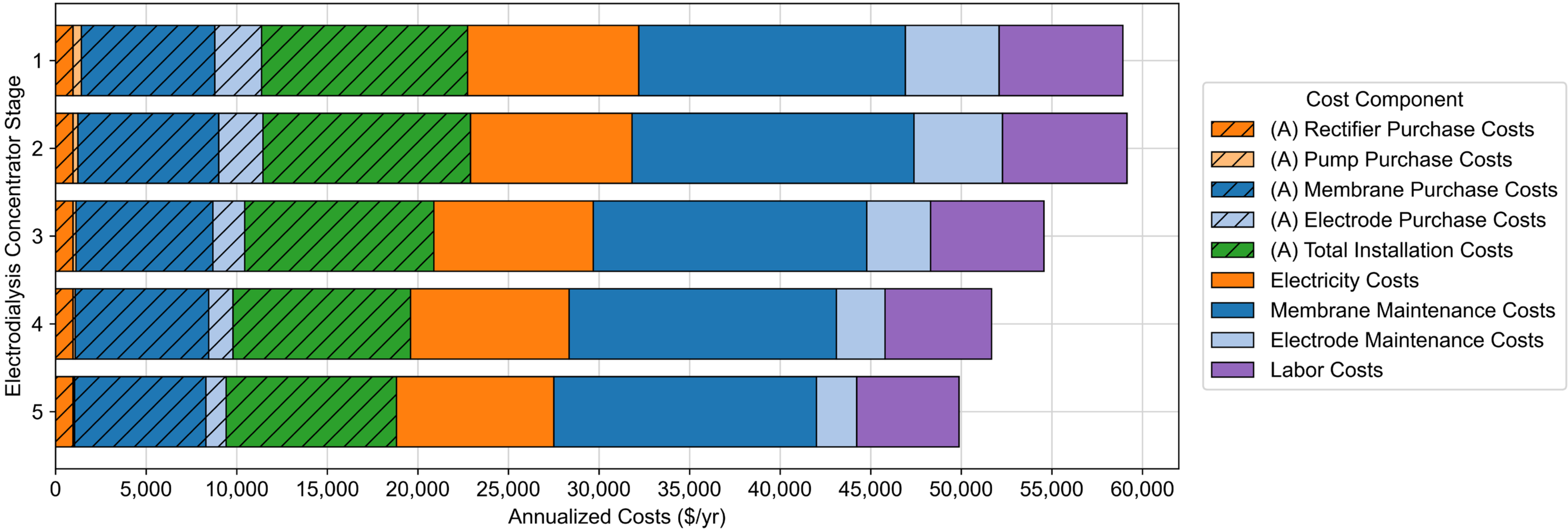
EDBC System Optimization Results and Conclusions

- Economic breakdown of annualized capital (A) and operating costs by type and stage
- **The performance and cost of the EDBC system is comparable to other desalination methods**
  - Promising results for EDBC as a high-salinity desalination technology
  - Provisional operation setpoints for EDBC pilot systems



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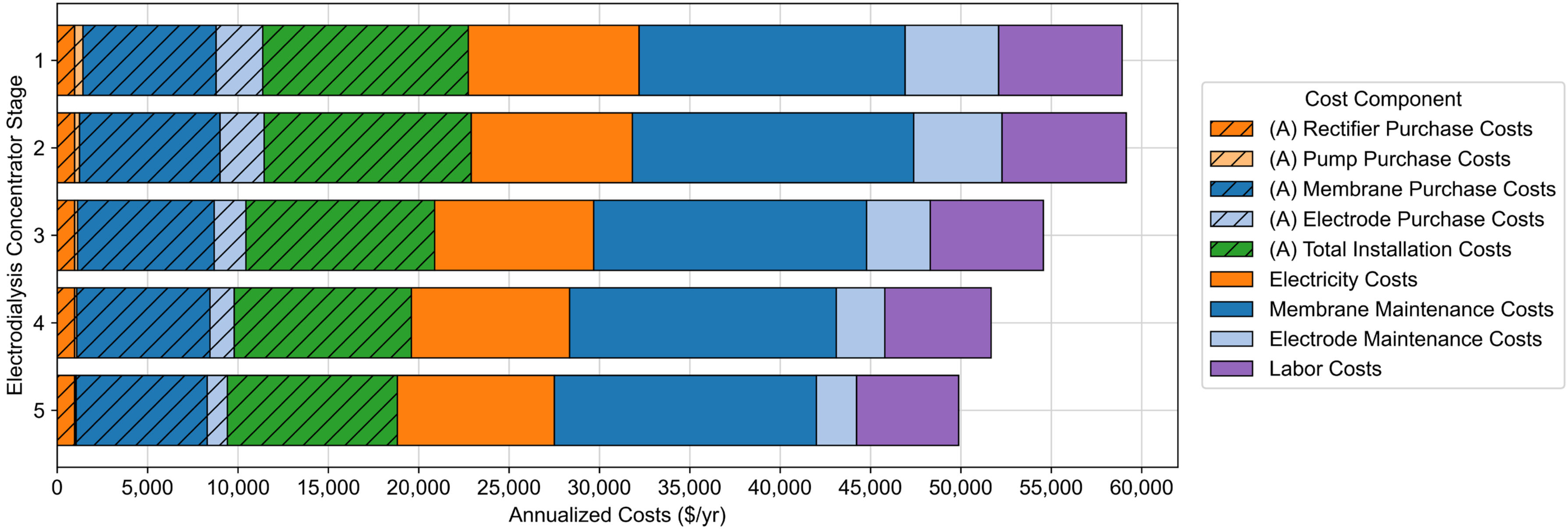
EDBC System Optimization Results and Conclusions

- Future efforts could extend analysis to further provide information on EDBC performance
  - Include recycle and bypass in process optimization
  - Study the effects the technoeconomic model parameters have on results and conclusions
  - Explore industrial economies of scale by contributing to costing methodology
  - Incentivize further treating diluate to design a process with zero-liquid discharge (ZLD)



Disclaimers

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Questions

Presenting Author: Hunter Barber (WVU)

Electrodialysis Collaborators: Srikanth Allu, Tim Bartholomew, Xiangyu Bi, Johnson Dhanasekaran, Fernando V. Lima (WVU), Abdiel Lugo (NMSU), Punhasa Senanayake (NMSU), Shane Walker (TTU), Pei Xu (NMSU)