ARPA-E Review: TEA Update

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November 11, 2021

Relevant Milestone

M2.1 TEA trade-off analysis on expended operational design space: Detailed TEA that allows precise quantitative target metrics for the following most critical drivers of overall system cost: electrodialyzer current density, electrodialyzer voltage, membrane contactor operating pH, membrane contactor CO_2 removal rate, and three different power generation sources (solar, solar-battery, grid assisted renewables). This ensures that target values for milestones are precise and will be used to inform future system designs.

TEA Outline

Overview & comparison to previous work

TEA Trade-Off Analysis:

1. Electrodialyzer current density & voltage
2. Power generation source
3. Membrane contactor vacuum level and CO_2 removal rate
4. Membrane contactor pH

Integration with thermodynamic system tradeoff analysis (M2.2)

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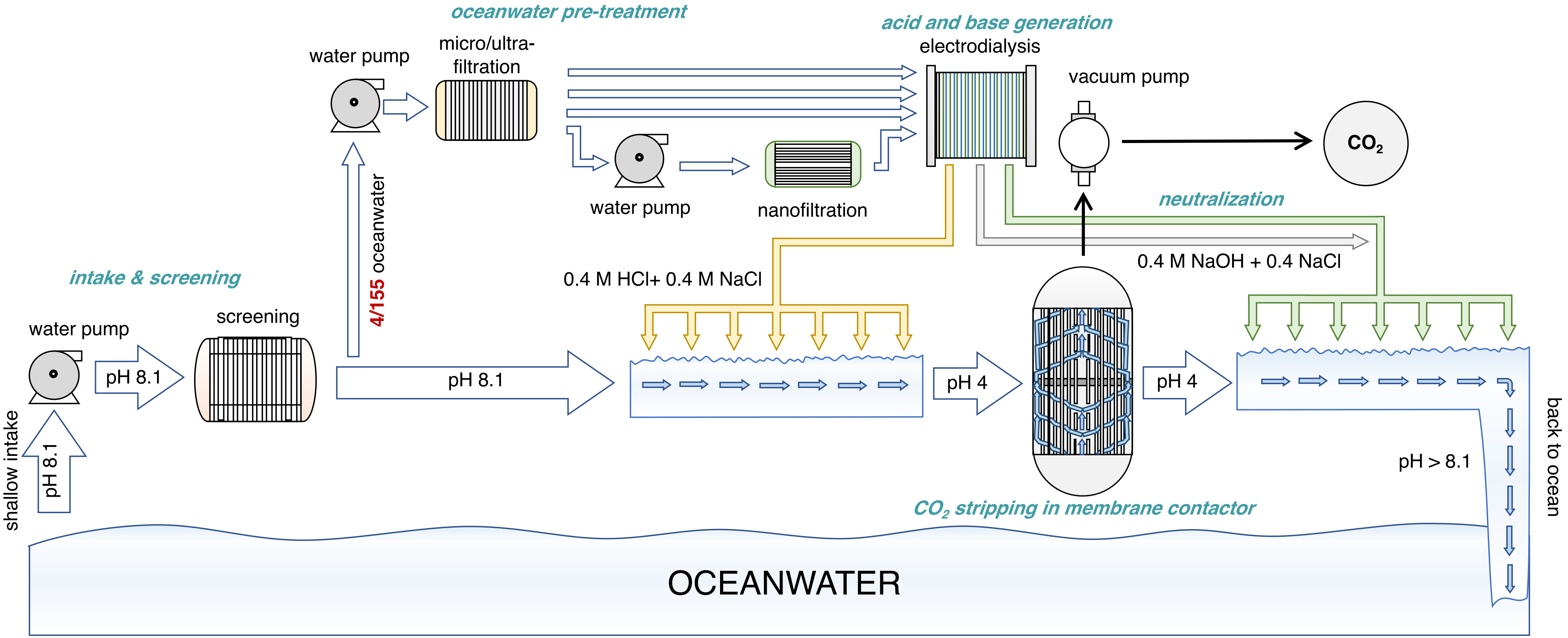
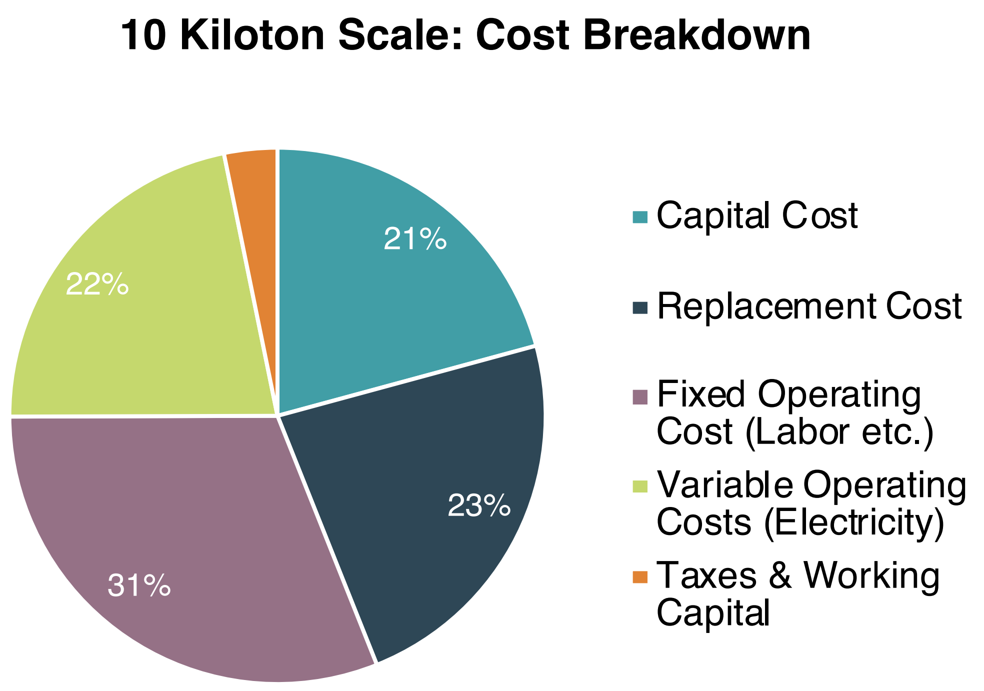
Current TEA is based on this system

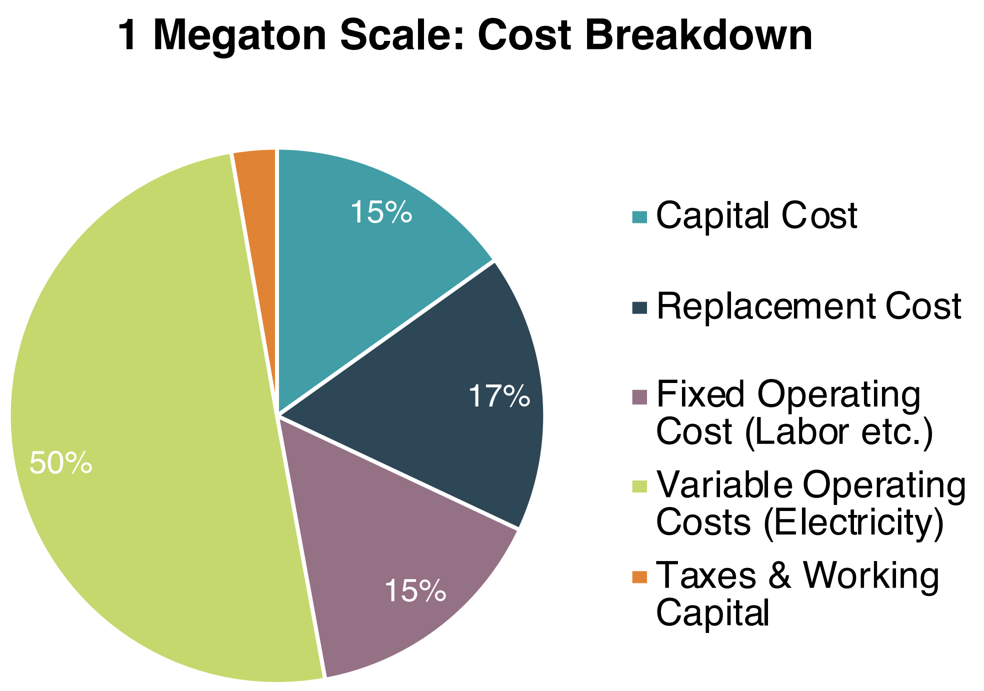


Key costs and parameter values

Item	Cost	Parameter	Value
Centrifugal pump (27,000 m^3/day)	$42,000	Oceanwater target pH**	4
Electrodialysis membrane cost	$0.05/$cm^2$	Membrane contactor efficiency	90%
Membrane contactor cost (1,920 m^3 oceanwater/day)	$6600	Electrodialyzer current density**	500 mA/cm^2
Vacuum pump cost (240,000 m^3/day)	$252,000	Electrodialyzer voltage**	2.5 V per cell
Intake piping* (400,000 m^3/day)	$420,000	Liquid ring vacuum pump base pressure**	35 Torr
Microscreening* (400,000 m^3/day)	$3,247,000	Scale	10 kiloton/yr (**current**) 1 megaton/yr (**future**)
Microfiltration* (10,000 m^3/day)	$1,555,000	Electricity price	$0.04/kWh (**current**) $0.02/kWh (**future**)
Nanofiltration (3,000 m^3/day)	$135,000	Labor cost (12.5 full-time employees at 10-kiloton/yr scale)	$40,000/year average salary

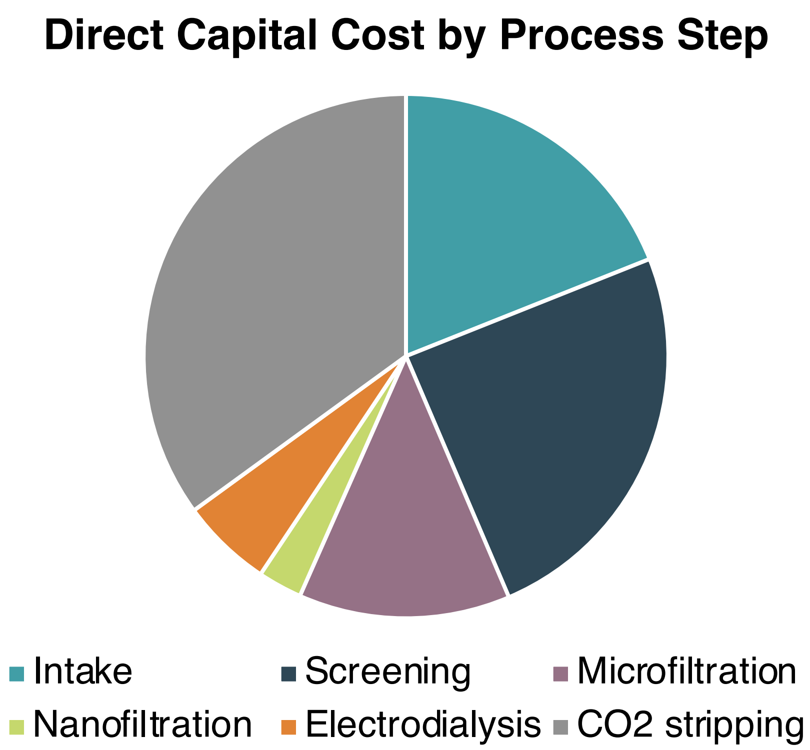
Current cost is **\$537/ton,** future cost is **\$117/ton CO_2**

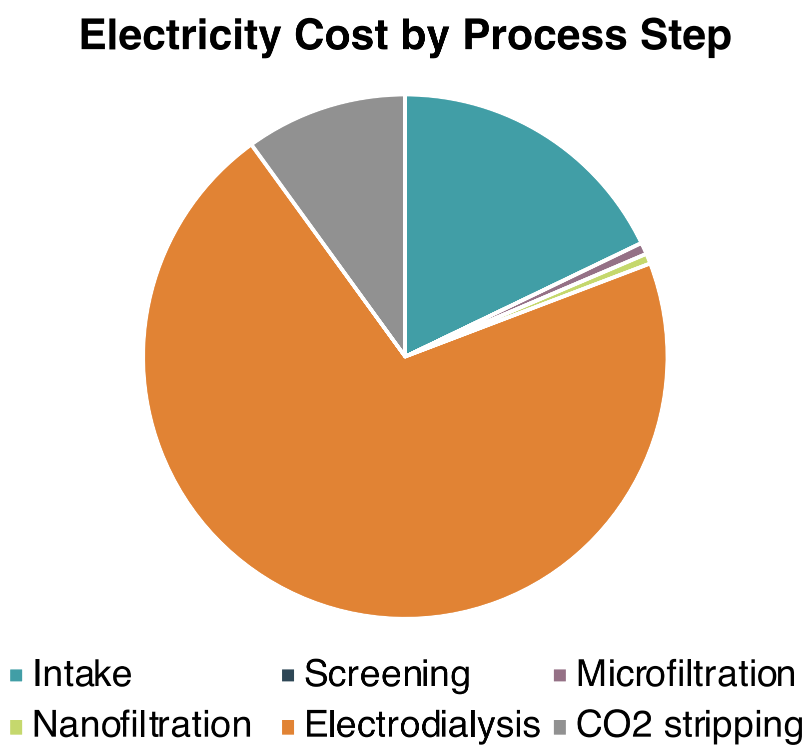




→ CapEx scales according to 6/10 rule, so becomes less significant at larger scales

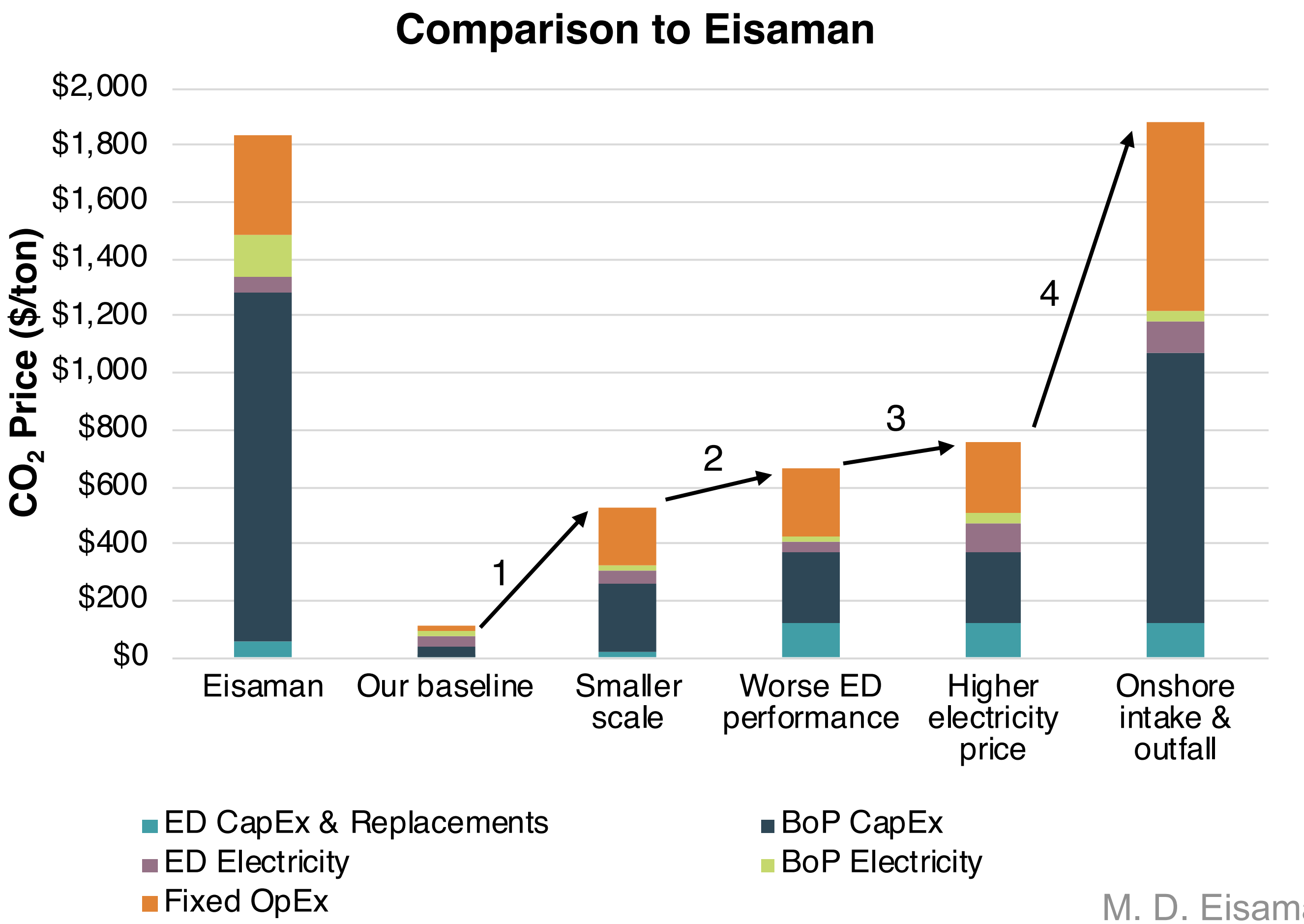
CO_2 stripping dominates CapEx, electrodialysis electricity dominates OpEx





→ Within each category (CapEx vs. electricity), breakdown by process step is the same at different scales

We achieve much lower CO_2 prices than previous papers (Eisaman *et al*) mostly due to larger scale, offshore intake



1. **Scale**
   1 megaton/year (us) → 7700 tons/year (them)

2. **Electrodialyzer current density**
   500 mA/cm^2 (us) → 100 mA/cm^2 (them)

3. **Electricity cost**
   $0.02/kWh (us) → $0.04/kWh (them)

4. **Intake/outfall**
   20x higher intake/outfall costs due to onshore intake & outfall

M. D. Eisaman *et al.*, *Int. J. Greenh. Gas Control*. **70**, 254–261 (2018)

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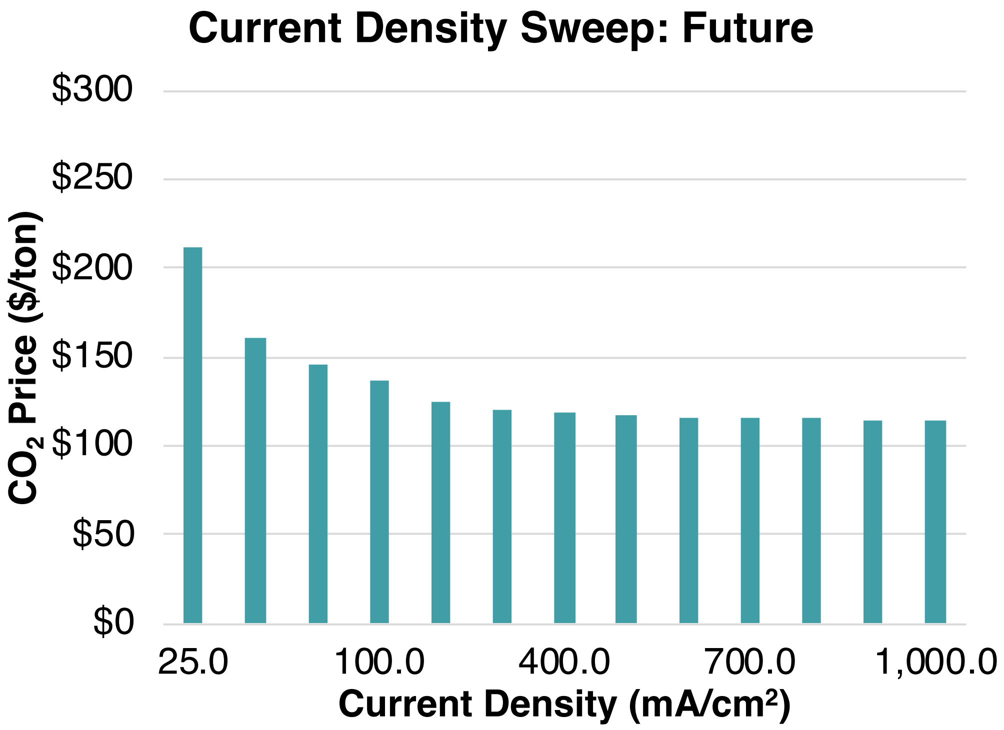
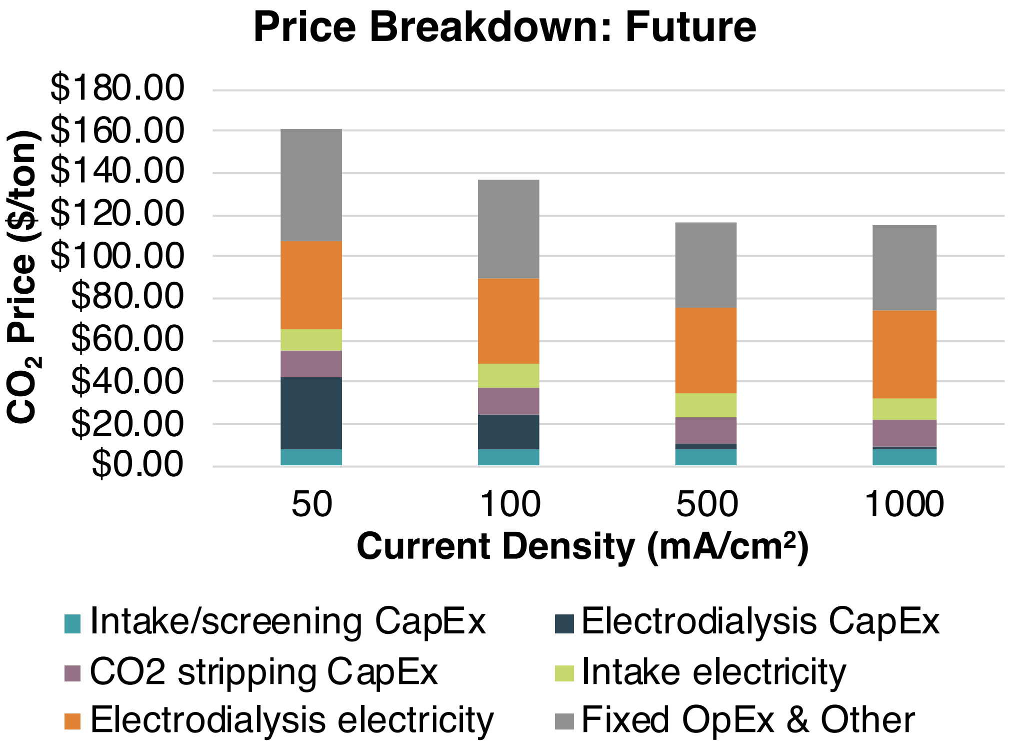
Integration with thermodynamic system tradeoff analysis (M2.2)

Diminishing returns to increasing current density above 500 mA/cm^2 at megaton scale

Current density only affects electrodialyzer CapEx, not OpEx

Above 500 mA/cm^2, electrodialyzer CapEx (dark blue bars) becomes negligible (same finding holds at 10-kiloton scale)

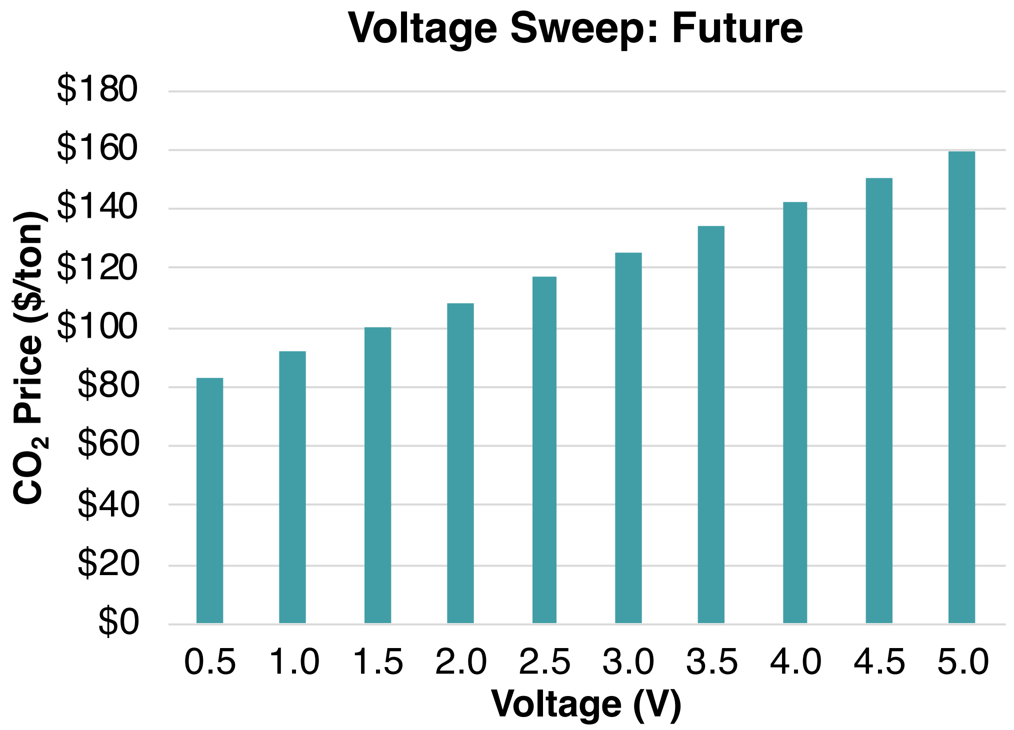


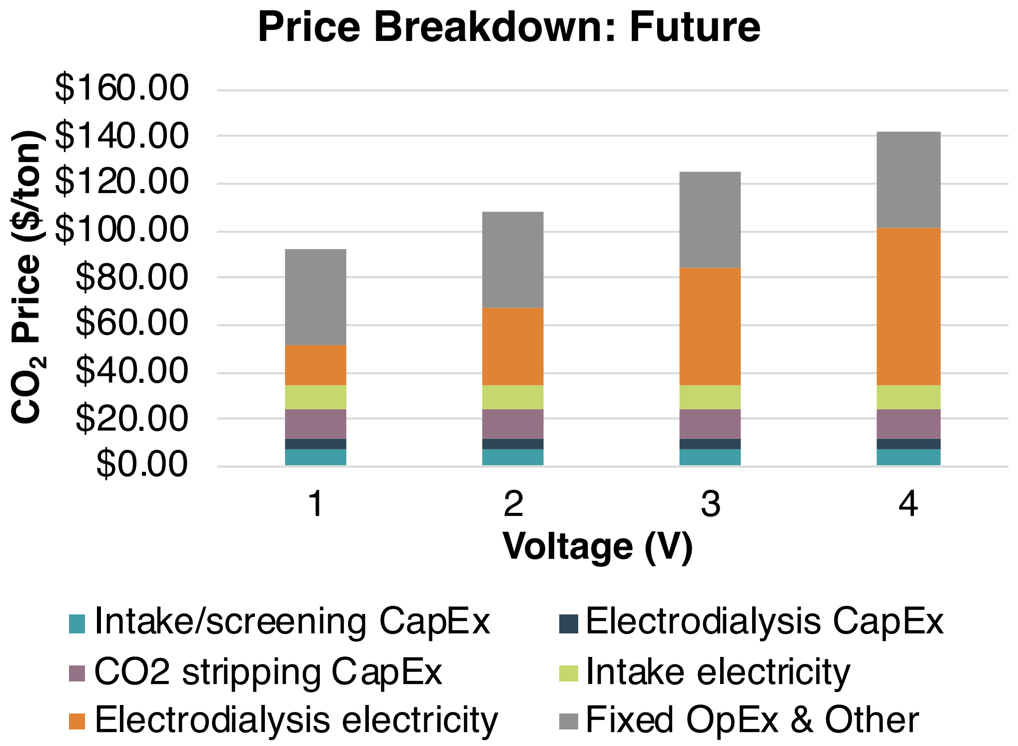


At megaton scale, reducing voltage reduces CO_2 price monotonically

Voltage only affects electrodialyzer OpEx, not CapEx

Electrodialyzer electricity price alone varies with voltage & remains significant down to 1 V (same finding holds at 10-kiloton scale)





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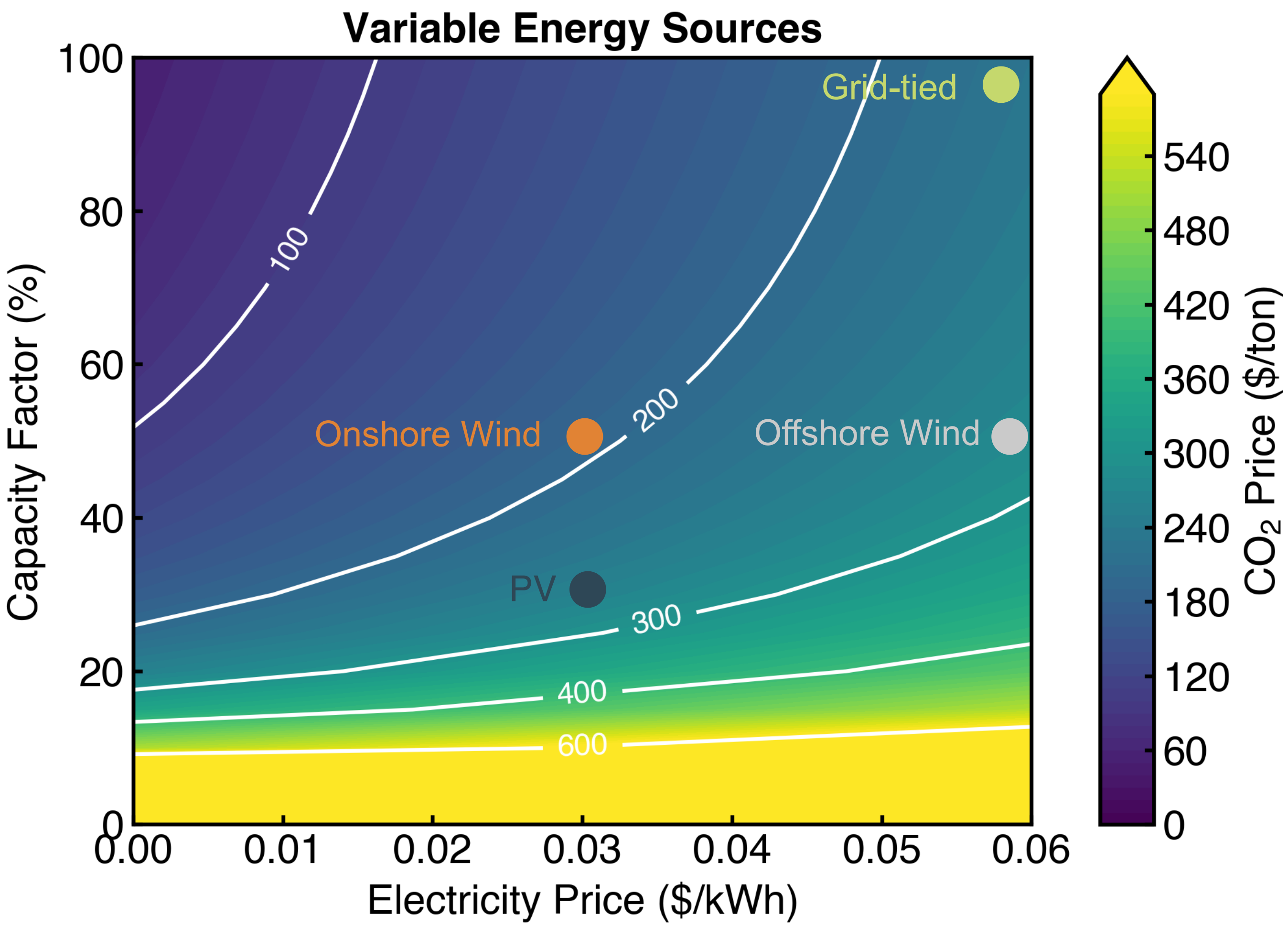
Integration with thermodynamic system tradeoff analysis (M2.2)

What if we have an electricity source that's almost free, but with a lower capacity factor?



- Renewables on grid may eventually lead to need for curtailment: using extra electricity when wind/solar are overproducing
- If electricity is free, we can have capacity factors as low as 50% and achieve less than $100/ton
- If we are paid to use electricity for optimizing grid load, we can have even lower capacity factors

Capacity factors & electricity prices from EIA Energy Outlook, NREL ATB, Lazard

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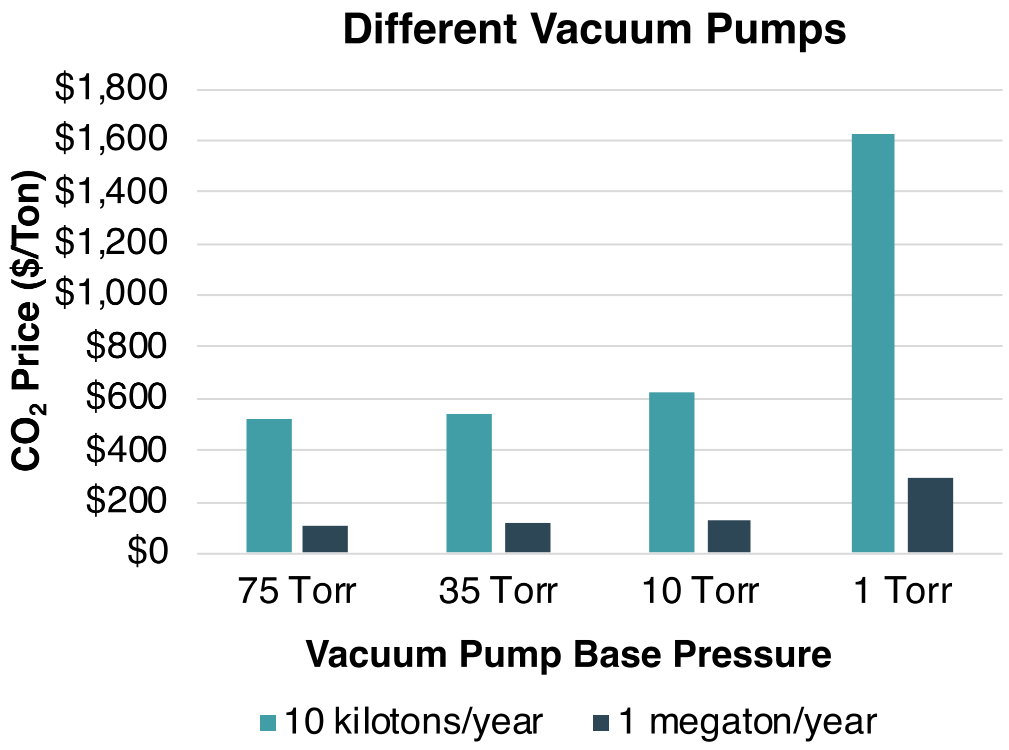
Integration with thermodynamic system tradeoff analysis (M2.2)

CO_2 cost is very sensitive to level of vacuum, because vacuum pumps have a maximum volumetric flow rate

- Most pumps have a maximum volumetric flow rate, since they are positive displacement pumps (remove a volume of gas over and over)
- At lower base pressures and the same **volumetric** flow rate, our **molar** flow rate becomes much smaller
- We need 10x as many pumps with the same max flow rate to get the same CO_2 throughput if we go from 10 Torr to 1 Torr
- Effect of increasing number of pumps becomes significant around 1 Torr



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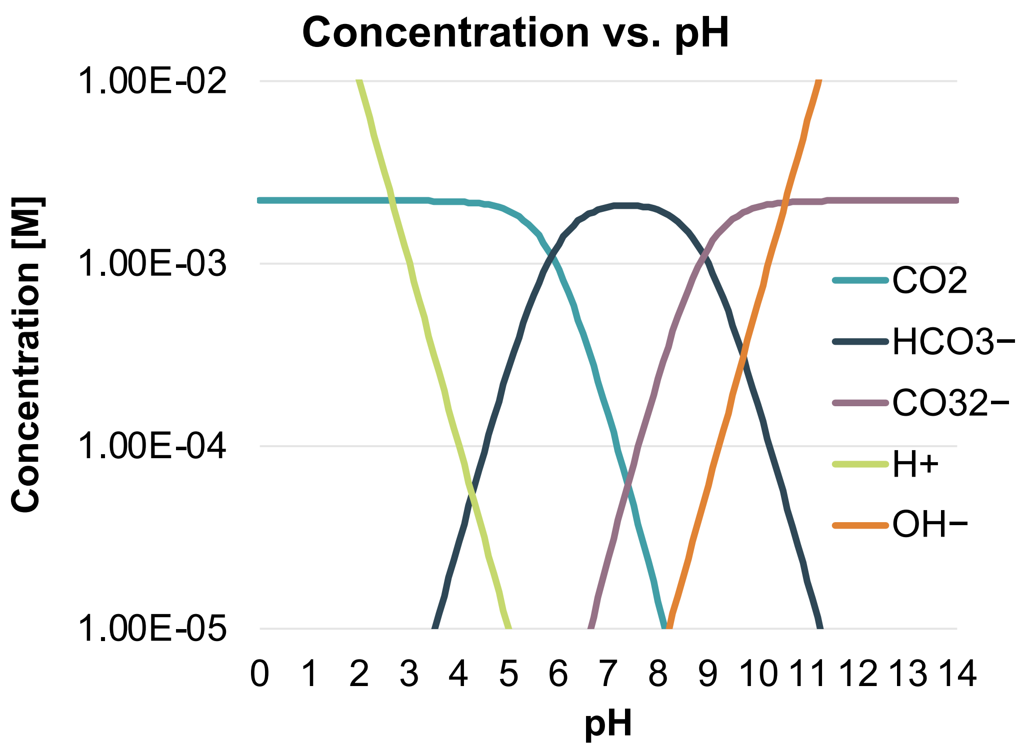
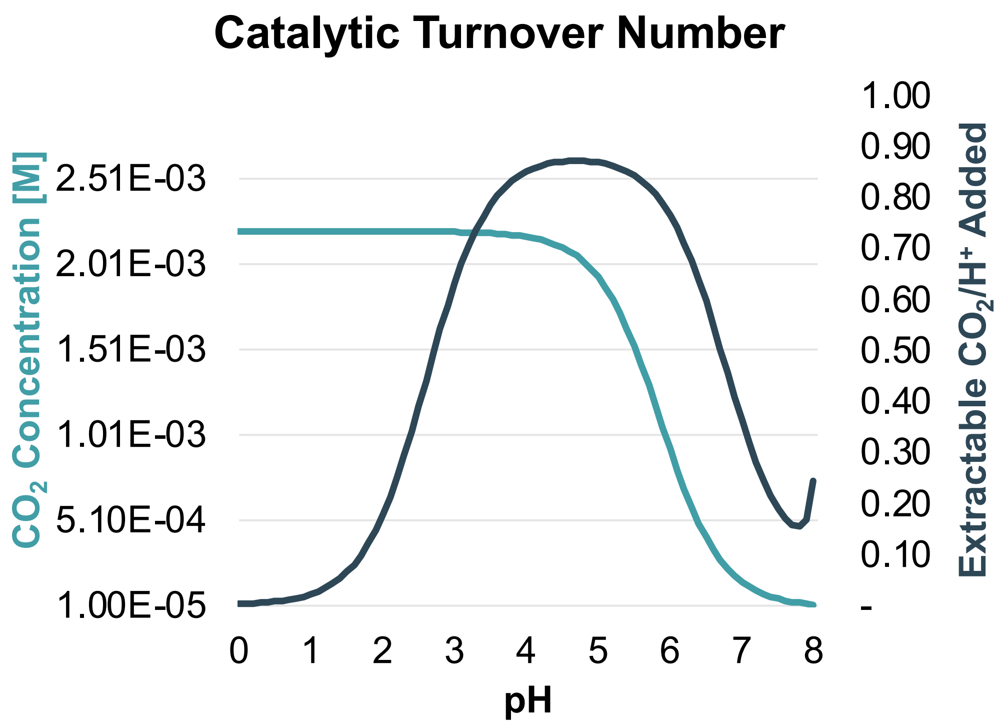
Integration with thermodynamic system tradeoff analysis (M2.2)

Key metric: catalytic turnover number, which is extractable CO_2 per H^+ added

Can also define a catalytic turnover factor $\mathrm{F_{CT}}$ that denotes the catalytic reaction rate enhancement

When extracting equilibrium concentration of CO_2(aq), $\mathrm{F_{CT}} = 1$. Otherwise, $\mathrm{F_{CT}}$ could be >1 or <1

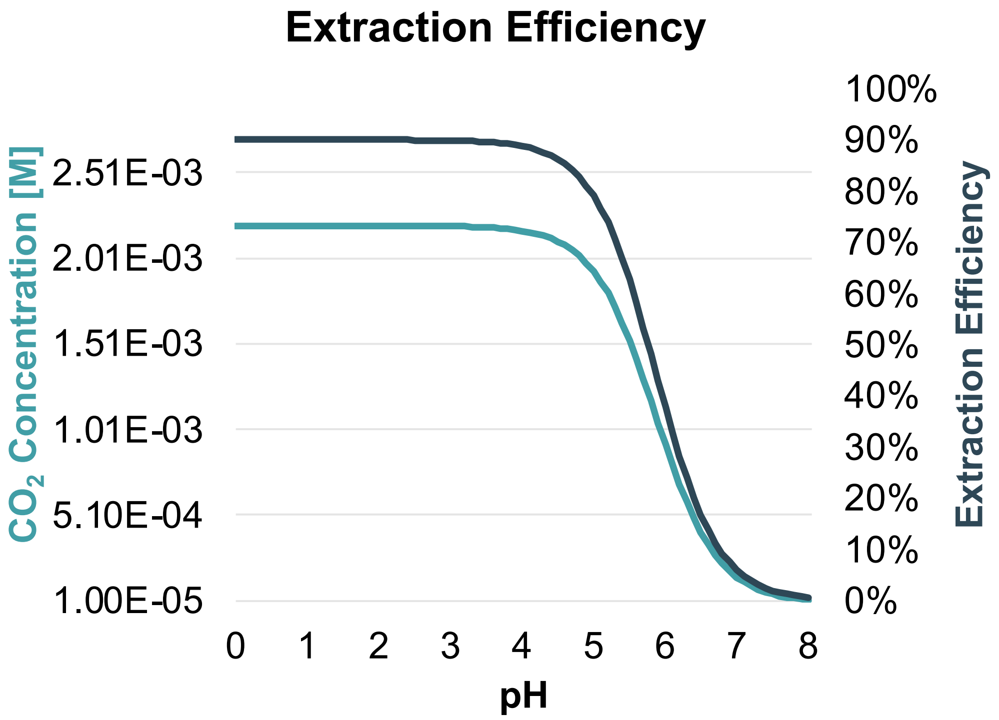


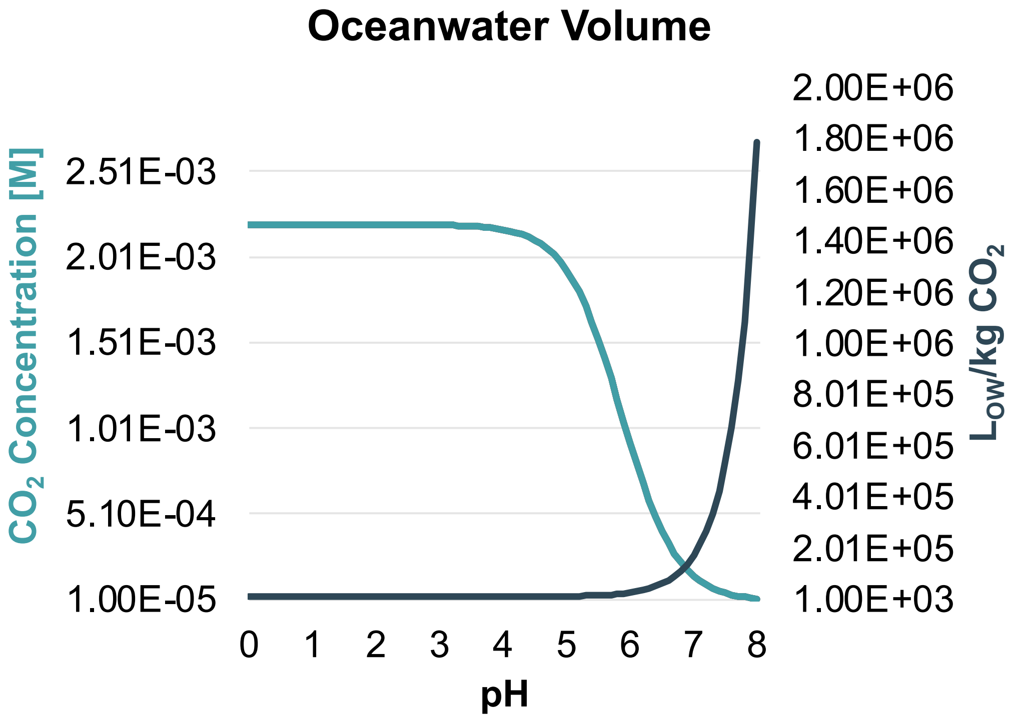


Extraction efficiency is CO_2 extracted per DIC in oceanwater

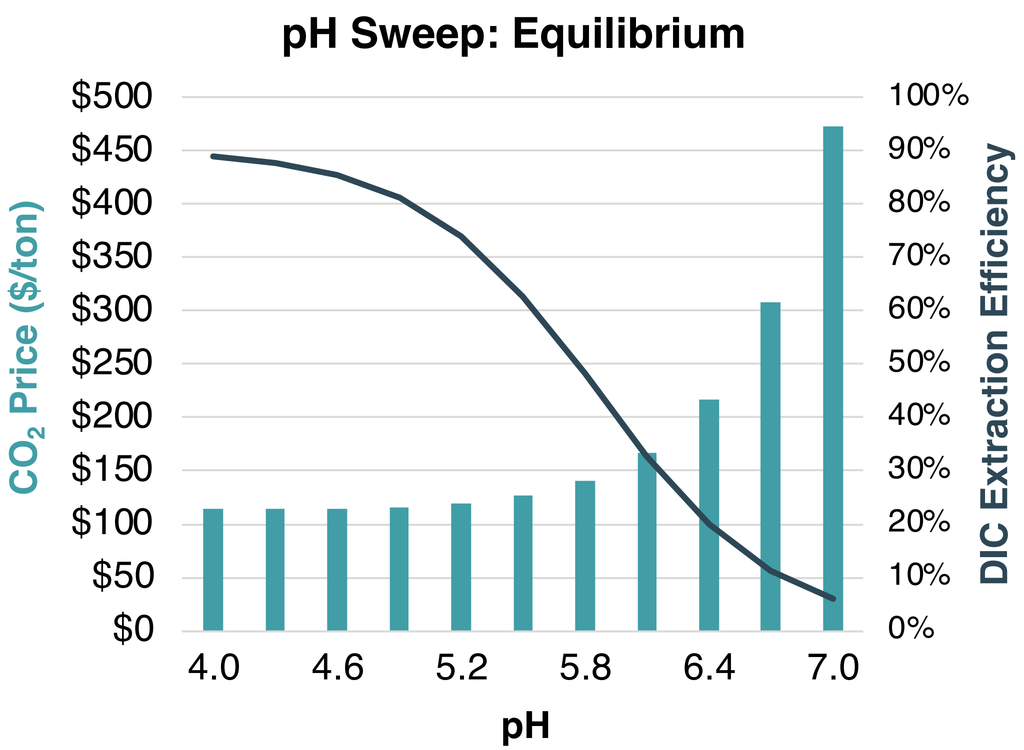
Equilibrium curves are shown here – pumping huge oceanwater volumes at higher pH

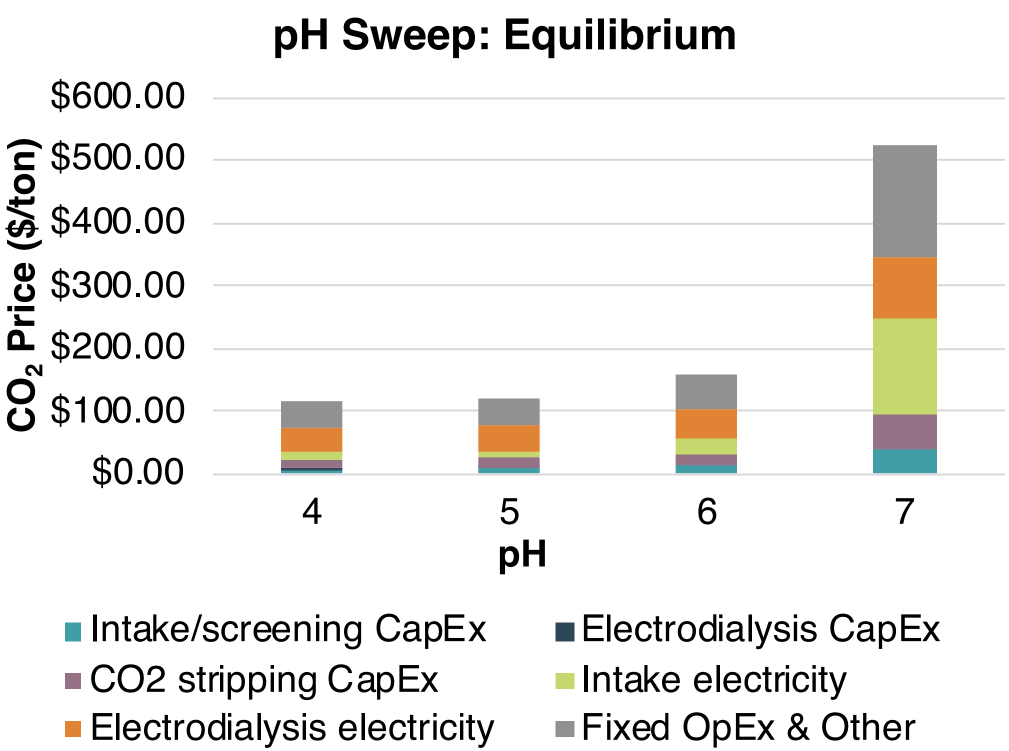
In steady-state or with catalysis, extraction efficiency could be enhanced by a factor equal to the “catalytic turnover factor”





Extracting the equilibrium concentration of CO_2 at a given pH, CO_2 price increases as pH increases

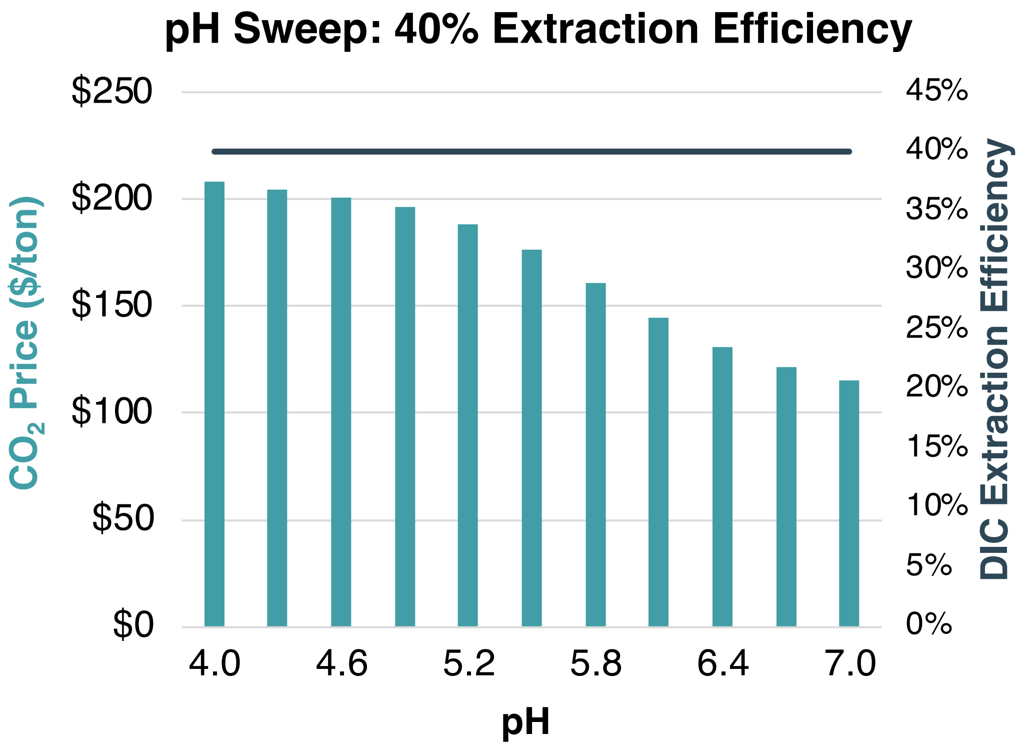


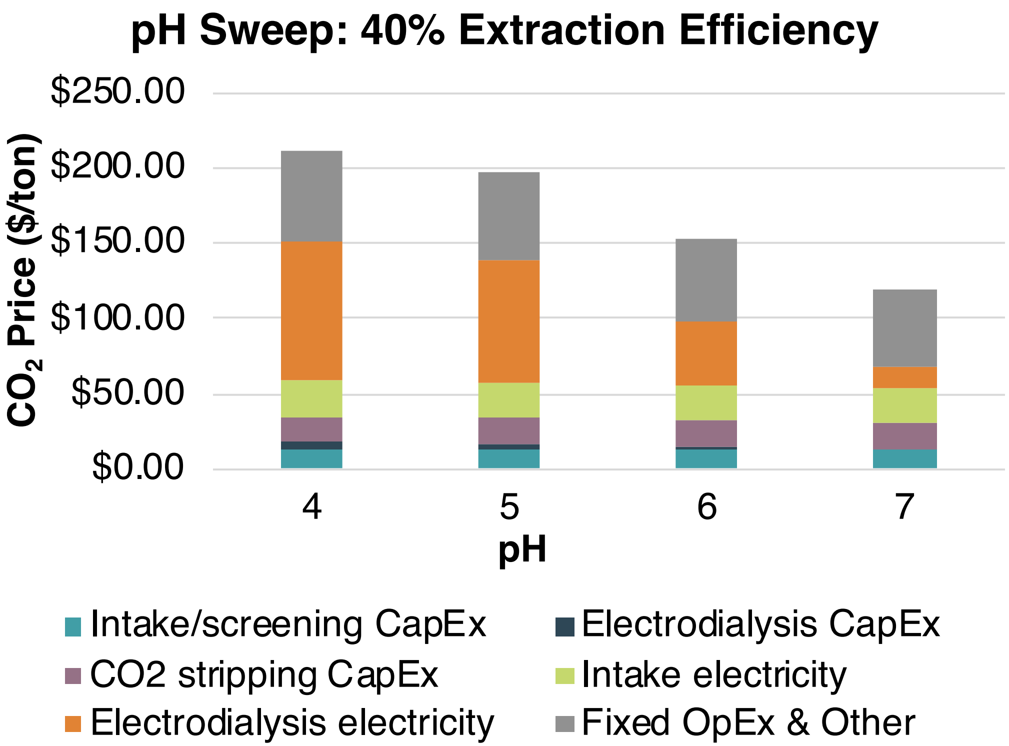


Due to decreased extraction efficiency

This mostly increases intake electricity costs (green bars) – at lower extraction efficiencies, we process more water

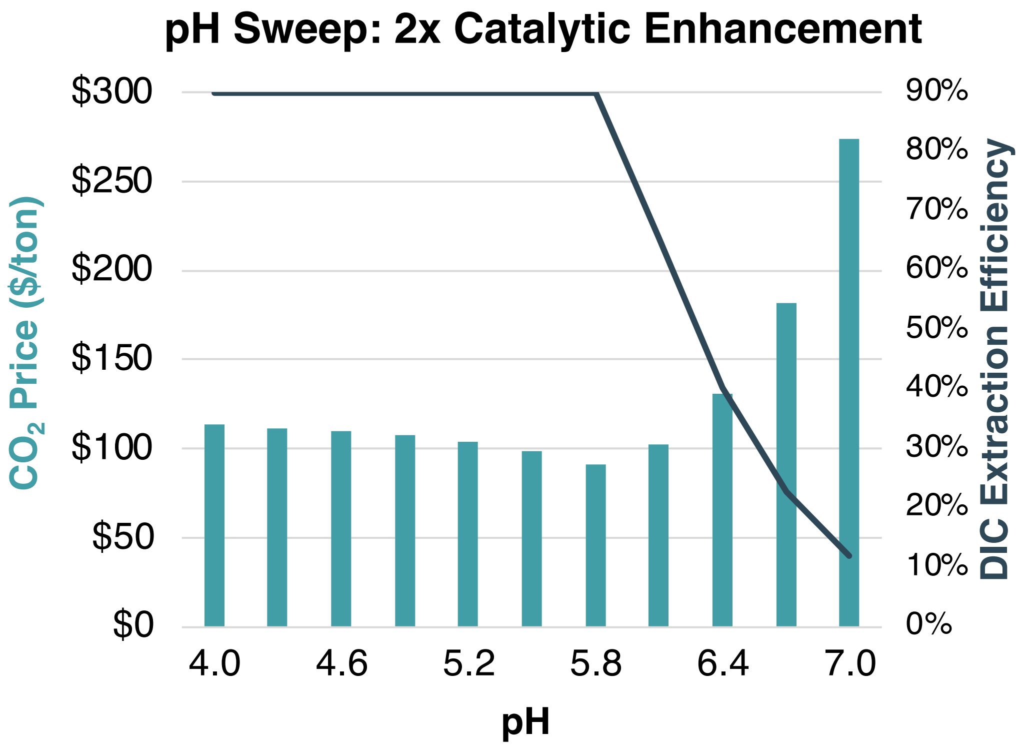
If we can achieve higher extraction efficiency at higher pH via catalysis, cost drops substantially

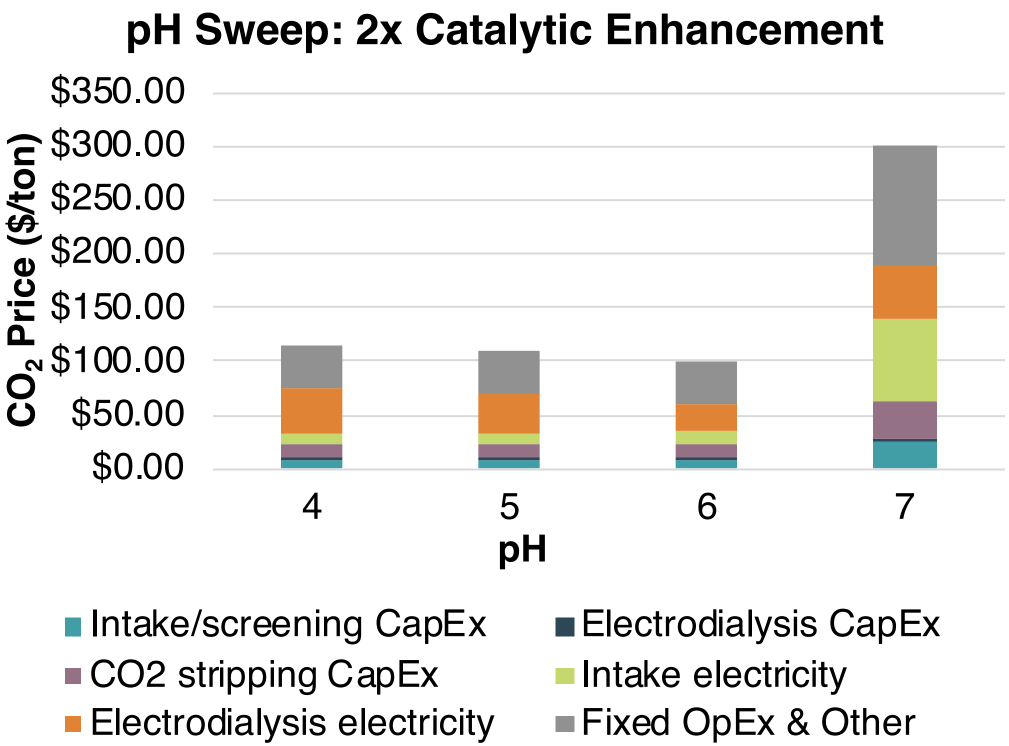




Price decreases as pH increases since we have to acidify a smaller fraction of the oceanwater through electrodialysis – leads to savings in electrodialysis electricity (orange bars)

Intermediate pH values between 4.0 and 8.1 are worth pursuing if we can achieve some small catalytic enhancement of CO_2 production





In this scenario, we have catalyzed CO_2 production by a factor of 2 (e.g. with a carbonic anhydrase mimic) and we can remove double the amount of CO_2 we could remove at equilibrium

This leads to lower CO_2 prices at intermediate pH (e.g. pH 6)

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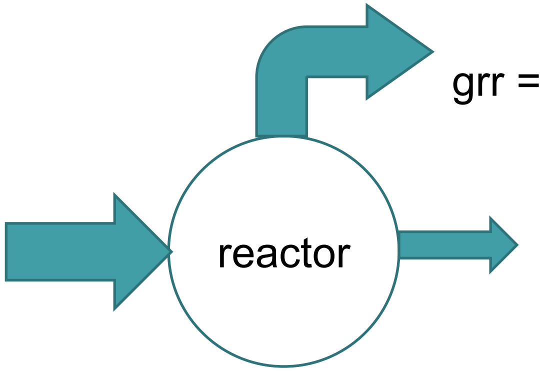
Relevant Milestone

M2.2 Thermodynamic system trade-off analysis: Perform thermodynamic analysis of dissolved CO_2 dependence on pH. Use the data to analyze tradeoff between the required pH shift (energy requirement for electrodialysis) vs. the required CO_2 partial pressure at the headspace over the saturated solution (energy requirement for vacuum pumping for CO_2 stripping).

0D reactor model in COMSOL allows us to model steady-state operation of our system (developed by Leanna @ UCI)

CO_2(g) flows out at
grr = gfr (s^{-1}) × $[CO_2(aq)]_{ss}$ (M)

H^+, OH^-, CO_2(aq), H_2CO_3,
and HCO_3^- flow in at
lfr (s^{-1}) × $[\text{species}]_{eq}$ (M)



H^+, OH^-, CO_2(aq), H_2CO_3,
and HCO_3^- flow out at
lfr (s^{-1}) × $[\text{species}]_{ss}$ (M)

Steady-state operation is important! Cannot assume we extract equilibrium concentration of CO_2

- Flowing oceanwater infinitely slowly → extract more DIC as CO_2, even at high pH
- Flowing oceanwater very quickly → cannot extract all dissolved CO_2(aq)

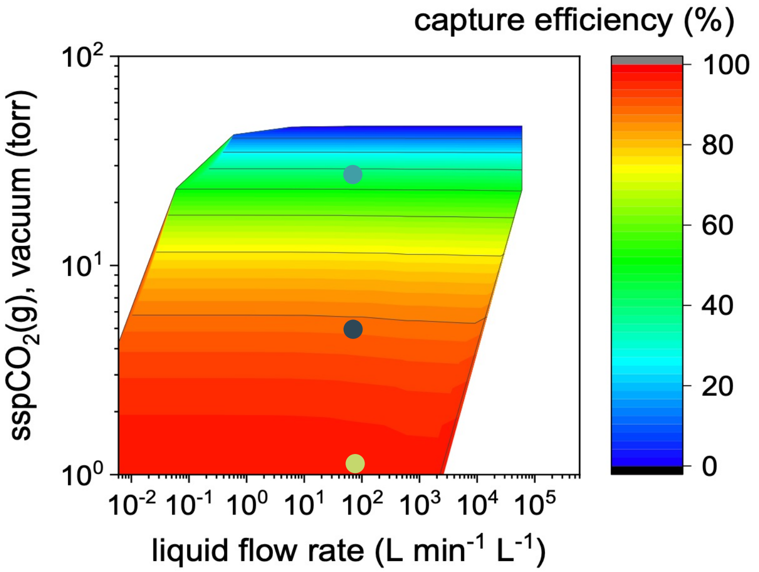
Lfr = liquid flow rate; Gfr = gas flow rate; Grr = gas reaction rate

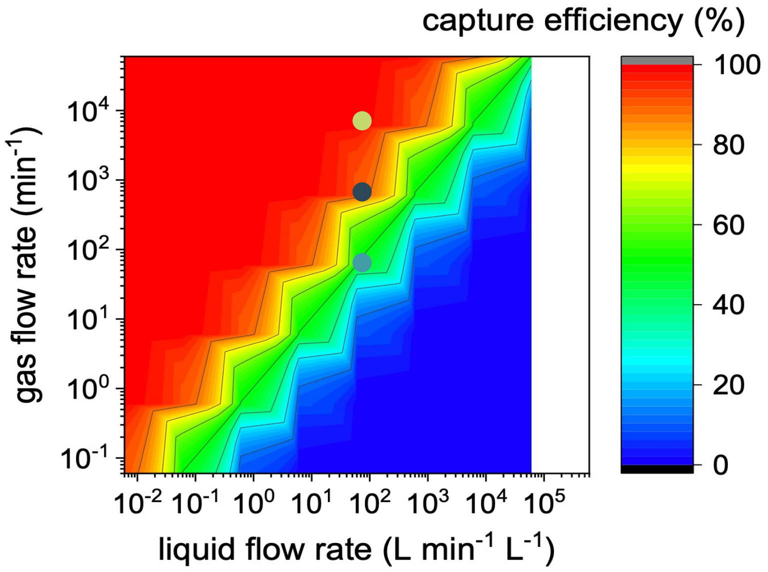
Output of the 0D reactor model can be used as input for our TEA

- **Extraction efficiency** (not liquid flow rate!) determines the necessary oceanwater flow rate for a given CO_2 scale
  - Want this to be high
- **CO_2 partial pressure** determines the vacuum base pressure in our membrane contactor
  - Want this to be high
- **Liquid flow rate** determines how many membrane contactors (MCs) we need
  - Want this to be within membrane contactor specs (10–100 L/min/L)

At pH 4, best operating point is close to 4 Torr, 91% extraction efficiency

Assuming equilibrium extraction, CO_2 price was lower ($115/ton)

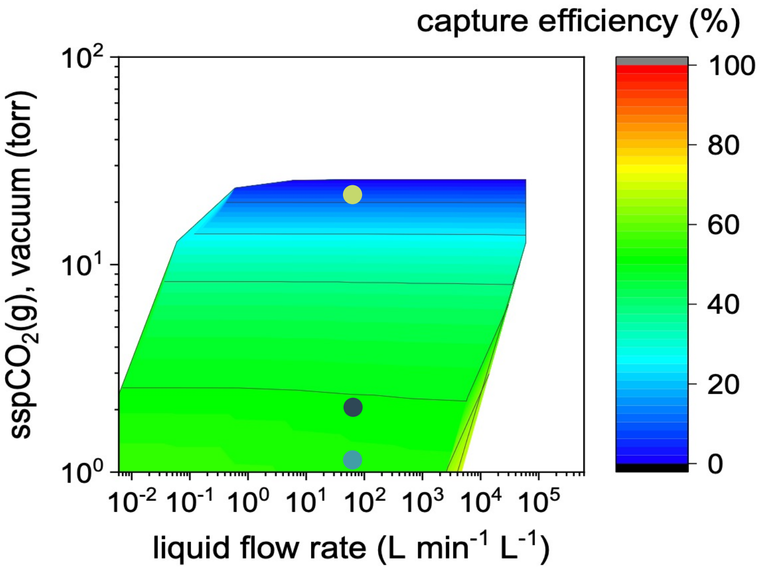


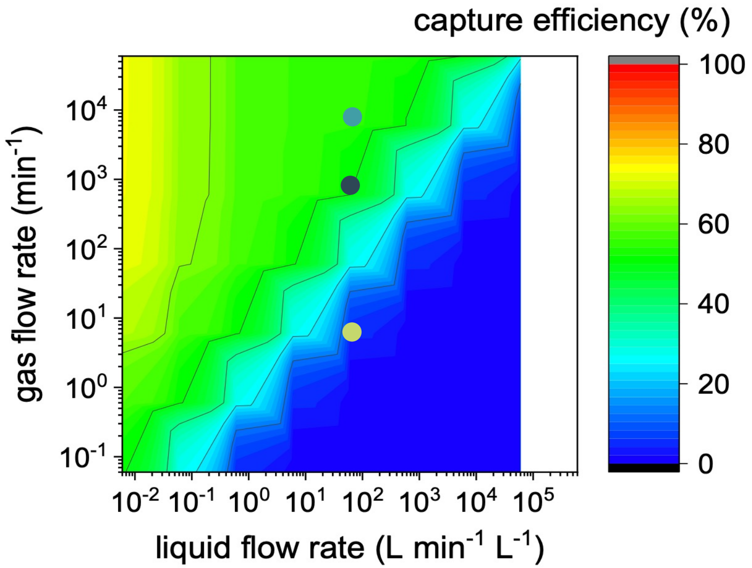


	pCO_2 (torr)	Extraction efficiency (%)	lfr (min^{-1})	gfr (min^{-1})	CO_2 Price
●	23	50	60	60	$178
●	4	91	60	600	$158
●	0.5	99	60	6000	$479

At pH 6, best operating point is close to 2 Torr, 50% extraction efficiency

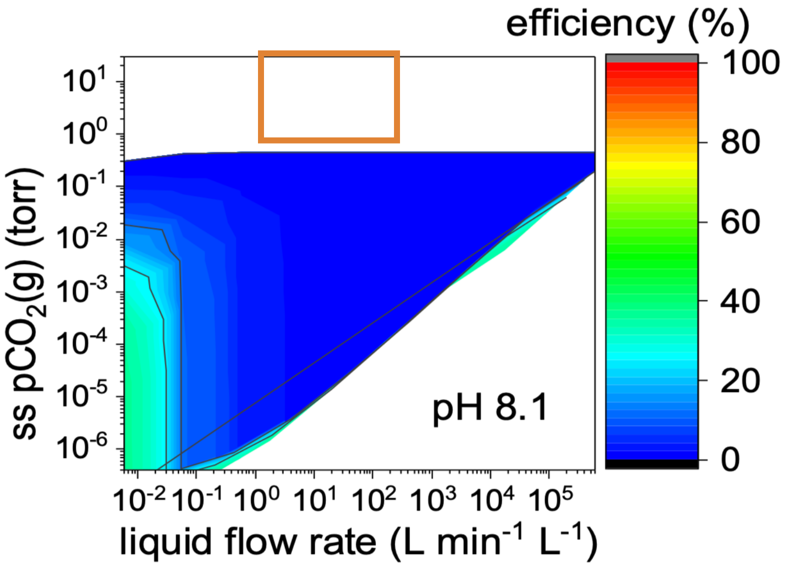
Assuming equilibrium extraction, CO_2 price was lower ($156/ton)

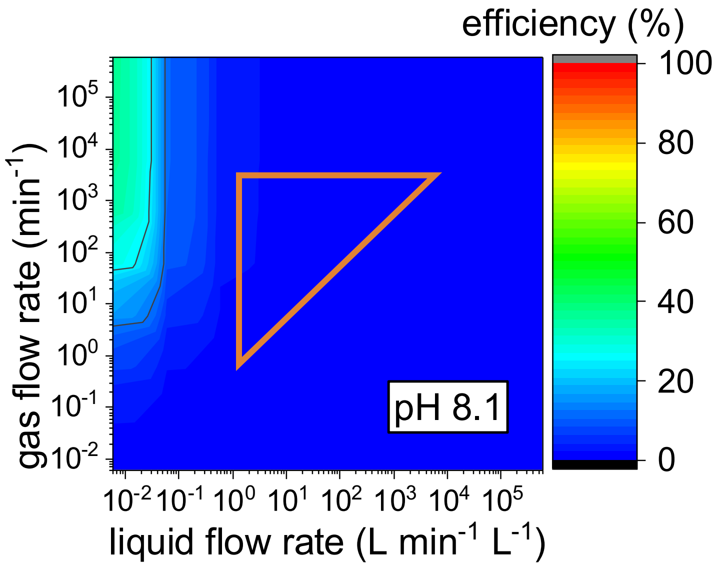




	pCO_2 (torr)	Extraction efficiency (%)	lfr (min^{-1})	gfr (min^{-1})	CO_2 Price
●	23	5	60	6	$805
●	2	50	60	600	$201
●	0.3	55	60	6000	$612

Operation at pH 8.1 is not realistic without catalysis





- Orange boxes mark target areas for low-cost operation
  - High pressure (equivalently, low gfr)
  - Gfr > lfr for high extraction efficiency
  - Lfr in membrane contactor operating range (1-100 min^{-1})
- Extraction efficiency low in those target areas – CO_2 price ends up being >$1000/ton

Main conclusions

- At 10 kiloton scale, CapEx and OpEx (mostly electricity) are both significant. At megaton scale, electricity cost dominates CO_2 cost.
- We achieve much lower costs than previous reports mostly due to 1) larger scale and 2) offshore floating platform reducing intake/outfall costs.
- CapEx is proportional to electrodialyzer current density, and OpEx is proportional to electrodialyzer voltage. Therefore, at megaton scale, we can tolerate lower current densities – diminishing returns to achieving greater than 500 mA/cm^2.
- If electricity is basically free, we can tolerate a lower capacity factor, as low as 50%.
- Vacuum level for pulling CO_2 off with membrane contactor must be greater than 1 Torr, otherwise we incur prohibitively large vacuum pump costs.
- Steady-state operation can yield different ideal operating points & a minimum cost operating point exists.