# Alkalinity Concentration Swing for Direct Air Capture of Carbon Dioxide


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# Carbon dioxide removal for **hard-to-avoid** emissions




**An estimate of the scale of hard-to-avoid emissions:**

**1.5-3.1** $GtCO_2$/yr

**CDRprimer.org: Section 1.4**



A Bergman & A Rinberg (2021) "The Case for Carbon Dioxide Removal: From Science to Justice“ **CDRprimer.org**

# A new DAC process based on concentrating the alkalinity of aqueous solution

# Atmosphere

Dissolved inorganic carbon (DIC) $= [CO_2]_{aq} + [HCO_3^-] + [CO_3^{-2}]$

Alkalinity $\approx [HCO_3^-] + \mathbf{2}[CO_3^{-2}]$

~420ppm

$CO_2$

$\updownarrow$

$CO_{2\,(aq)} + H_2O \leftrightarrow \underbrace{HCO_3^- + H^+ \leftrightarrow CO_3^{-2} + 2H^+}$

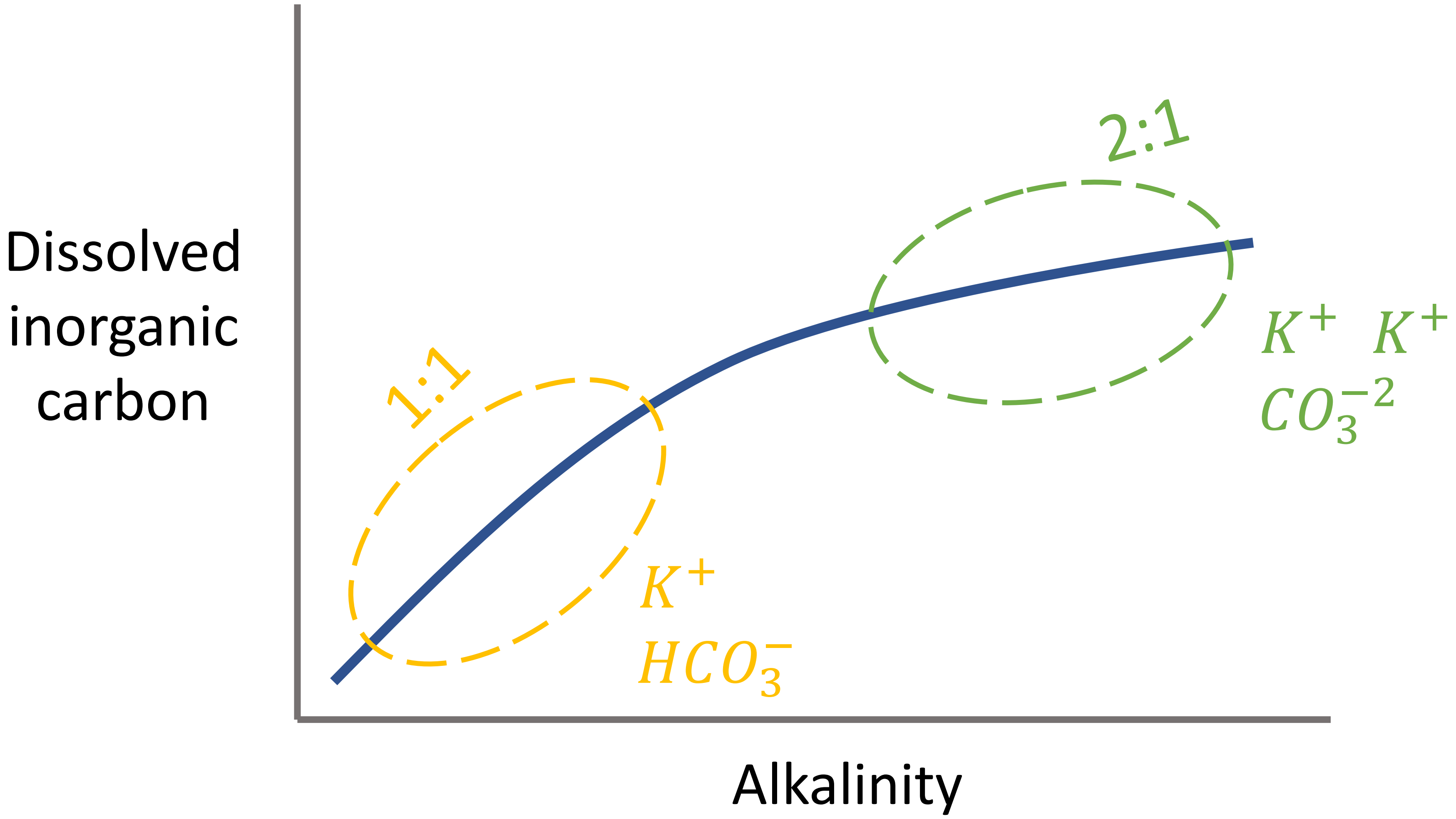
dissolved carbon dioxide (0.014 mM)

bicarbonate

carbonate

Function of **alkalinity** (e.g., $[K^+]$)

# The alkalinity concentration swing (ACS)






Rinberg*, Bergman*, Schrag, Aziz. **"Alkalinity Concentration Swing for Direct Air Capture of Carbon Dioxide."** ChemSusChem (2021)

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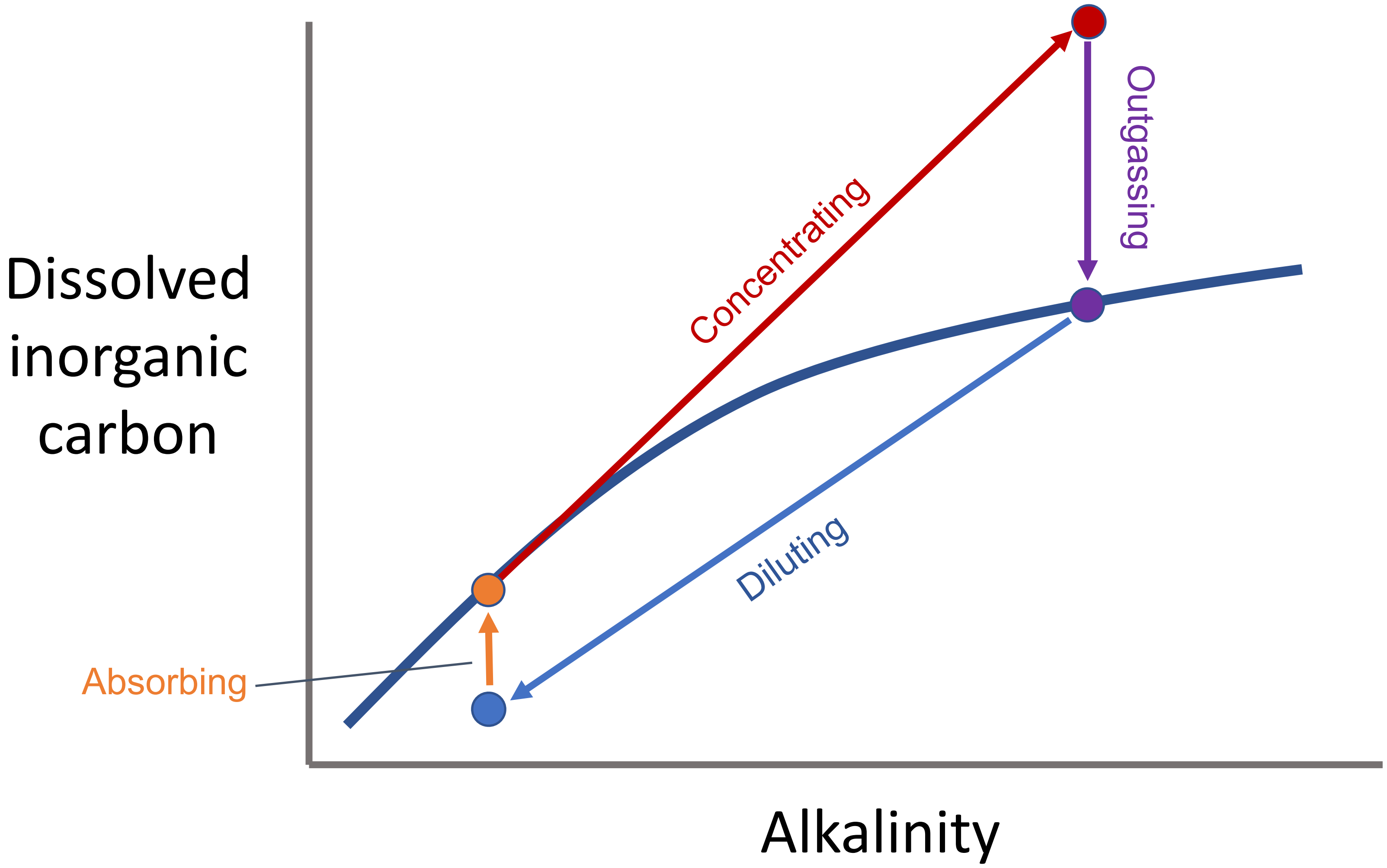




Rinberg*, Bergman*, Schrag, Aziz. **“Alkalinity Concentration Swing for Direct Air Capture of Carbon Dioxide.”** ChemSusChem (2021)

# Bicarbonate disproportionation reaction:

$$2HCO_3^- \rightarrow CO_2 + CO_3^{-2} + H_2O$$



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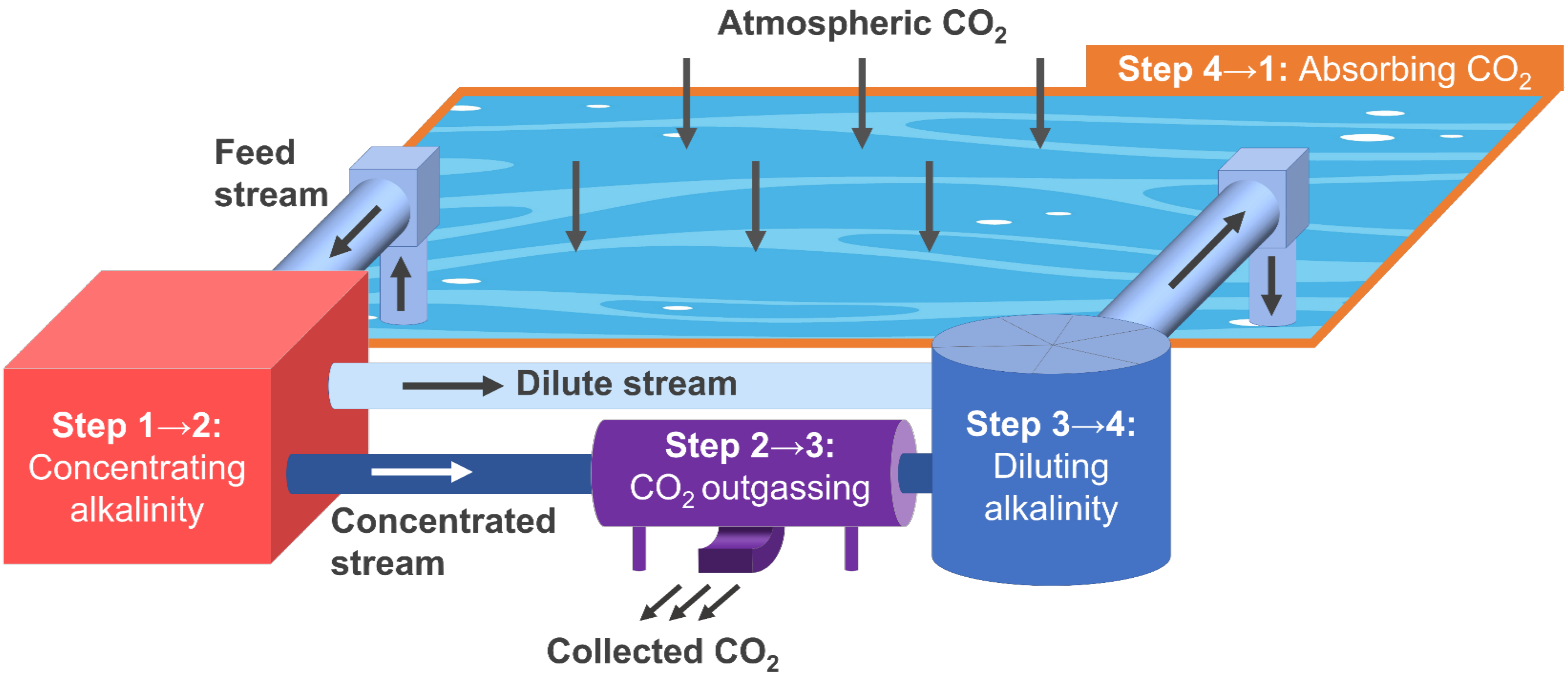
# ACS full system schematic




**Rinberg*, Bergman*, Schrag, Aziz**, "Alkalinity Concentration Swingfor Direct Air Capture of Carbon Dioxide." ChemSusChem (2021)

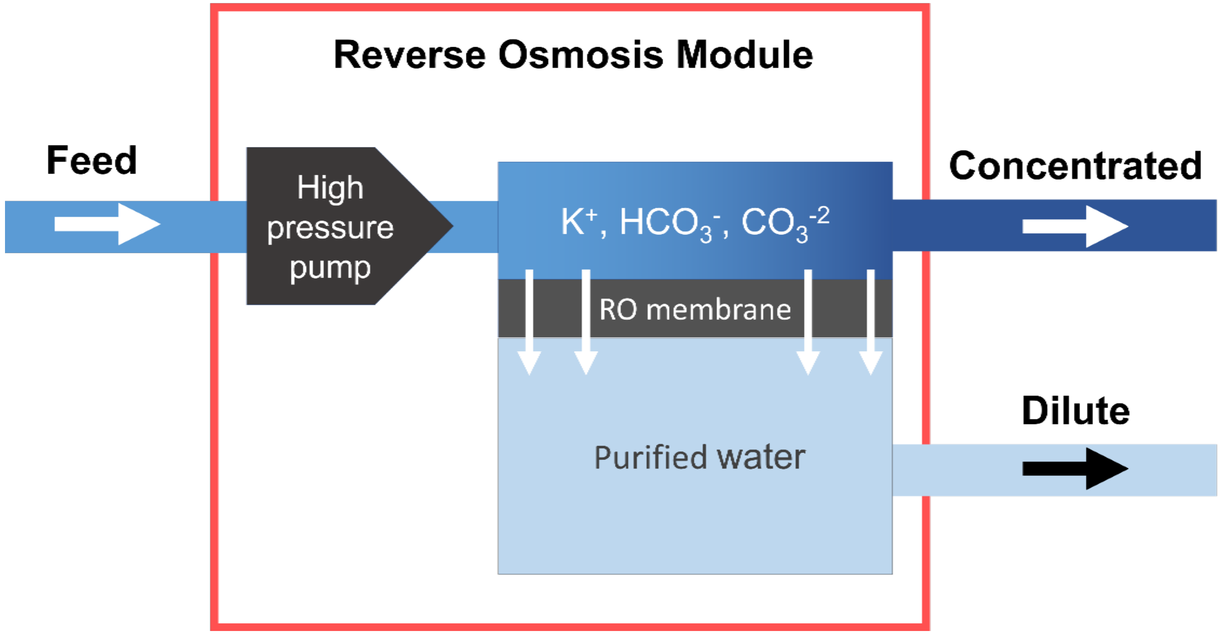
**Step 1→2:**
Concentrating
alkalinity

# We explore two implementations of the ACS:

1. **Reverse osmosis**
(pressure)

2. **Capacitive deionization**
(voltage)

# Using reverse osmosis for the alkalinity concentration swing

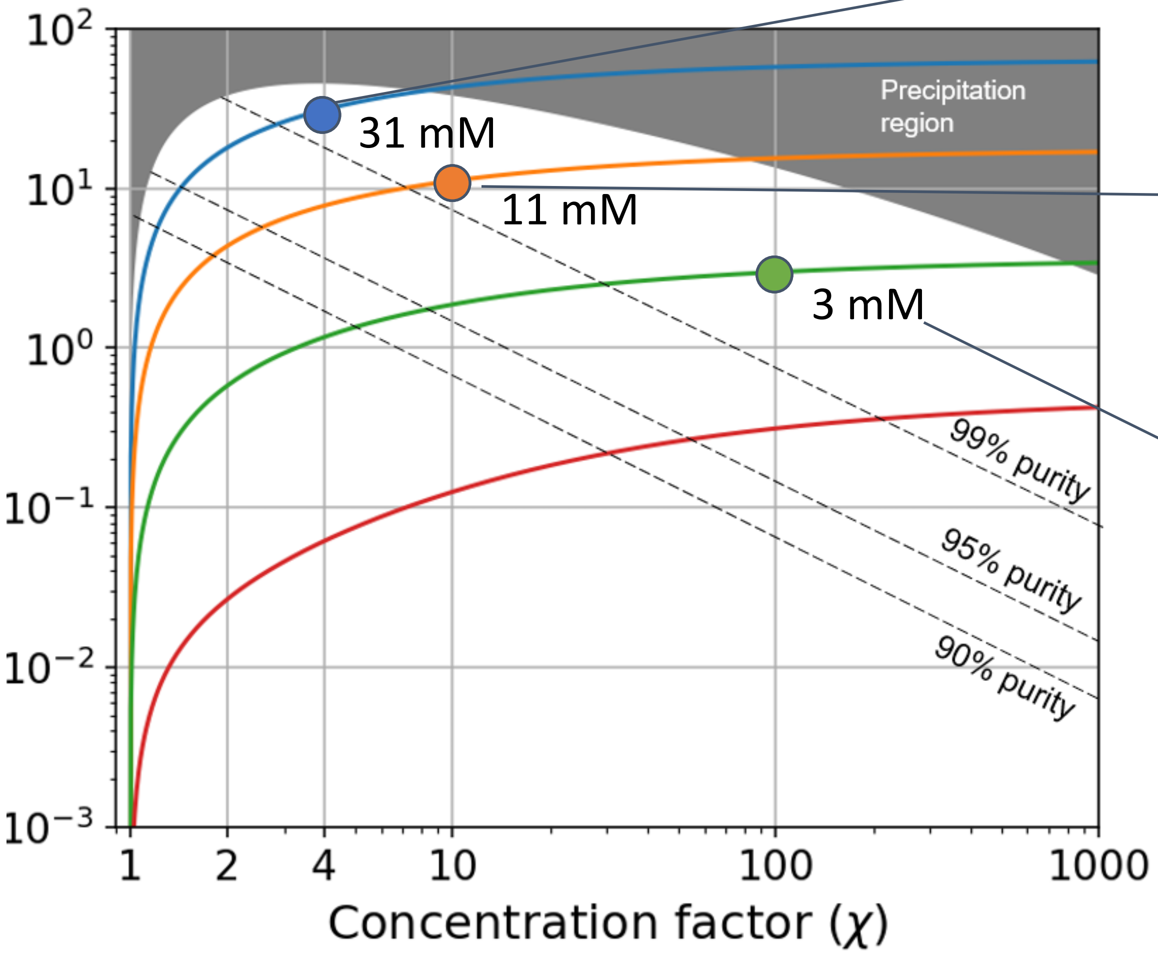



Globally, reverse osmosis produces
**35 billion cubic meters of water per year**

*Jones et al., 2019. "The State of Desalination and Brine Production: A Global Outlook"*

# ACS-RO: theoretical outgassing and energy

Carbon outgassed for capture (mM)




**Initial alkalinity:**

- $A_i = 1M$
- $A_i = 100mM$
- $A_i = 10mM$
- $A_i = 1mM$

1 → 4 M:
Outgassed: **31 mM**
ACS-RO: **350-420 kJ/mol**

0.1 → 1 M:
Outgassed: **11 mM**
ACS-RO: **190-220 kJ/mol**

0.01 → 1 M:
**Outgassed: 3 mM**
**ACS-RO: 160-190 kJ/mol**

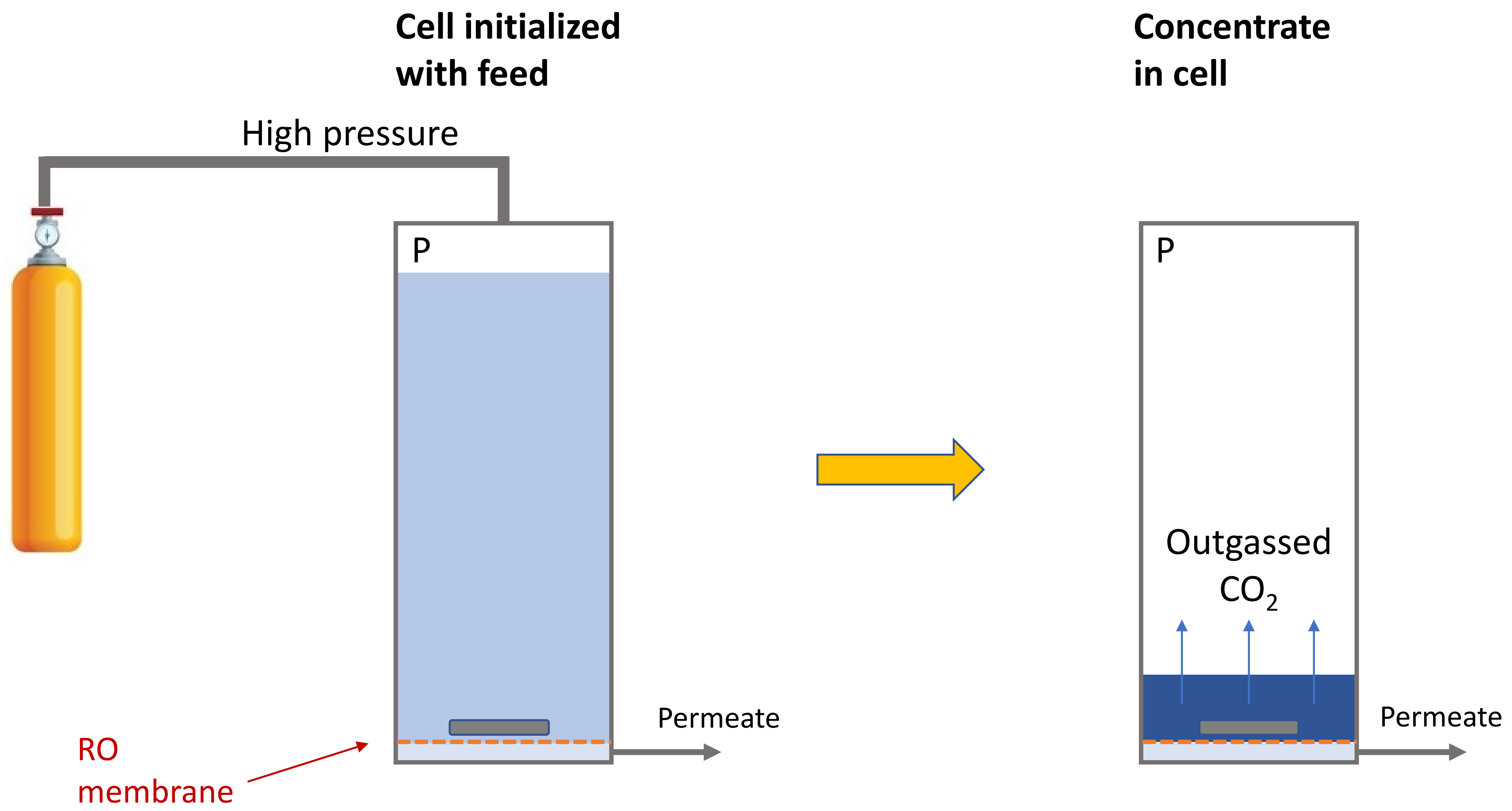
Carbon Engineering:

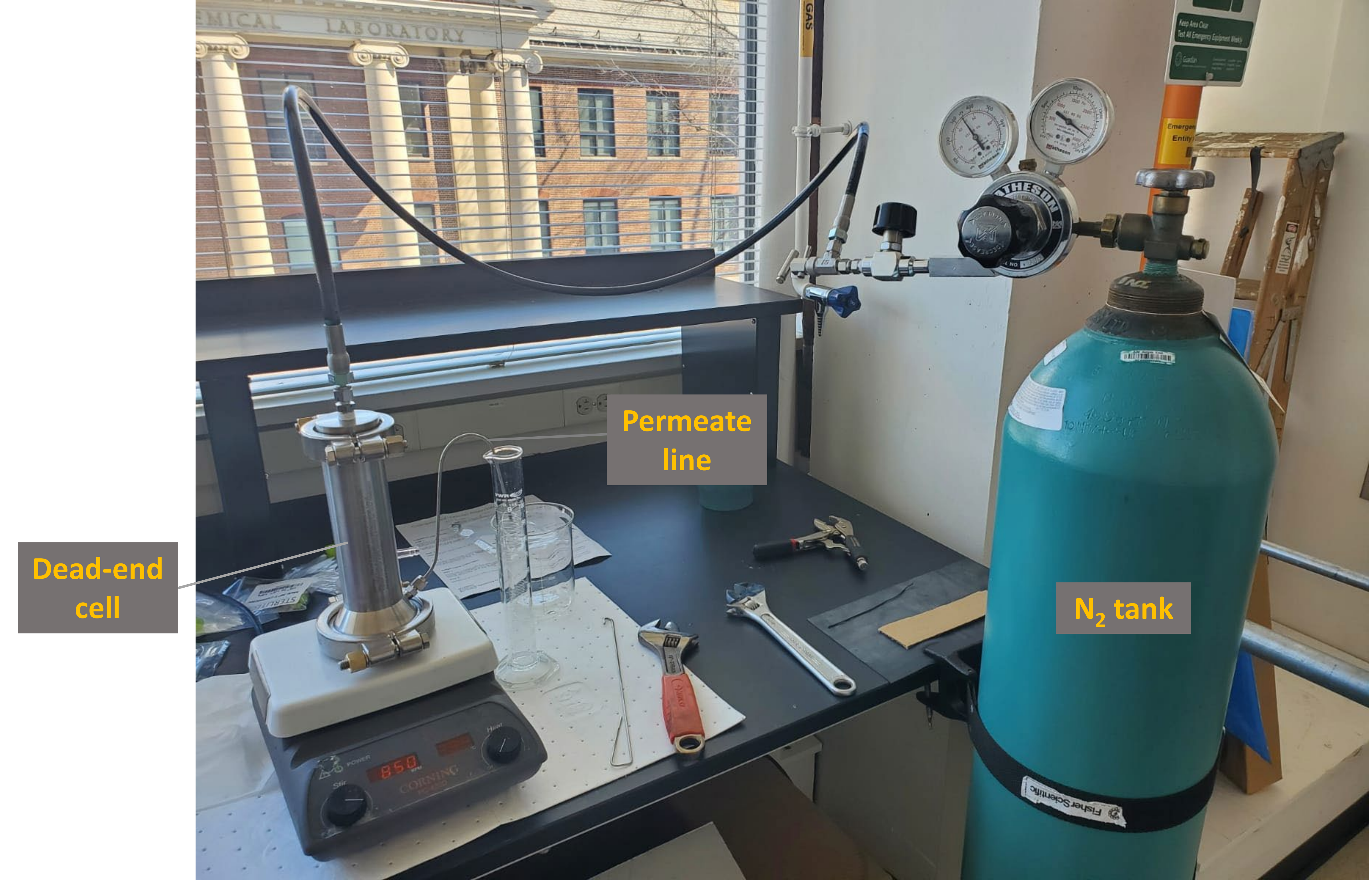
- 360-480 kJ/mol
- 81 mM extraction capacity



Rinberg*, Bergman*, Schrag, Aziz. **“Alkalinity Concentration Swing for Direct Air Capture of Carbon Dioxide.”** ChemSusChem (2021)

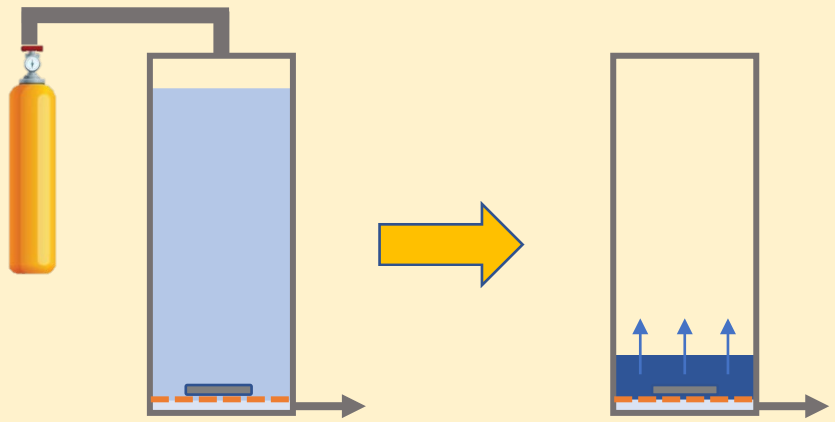
# Dead-end cell for preliminary concentration experiments




Dead-end cell
Permeate line
$N_2$ tank

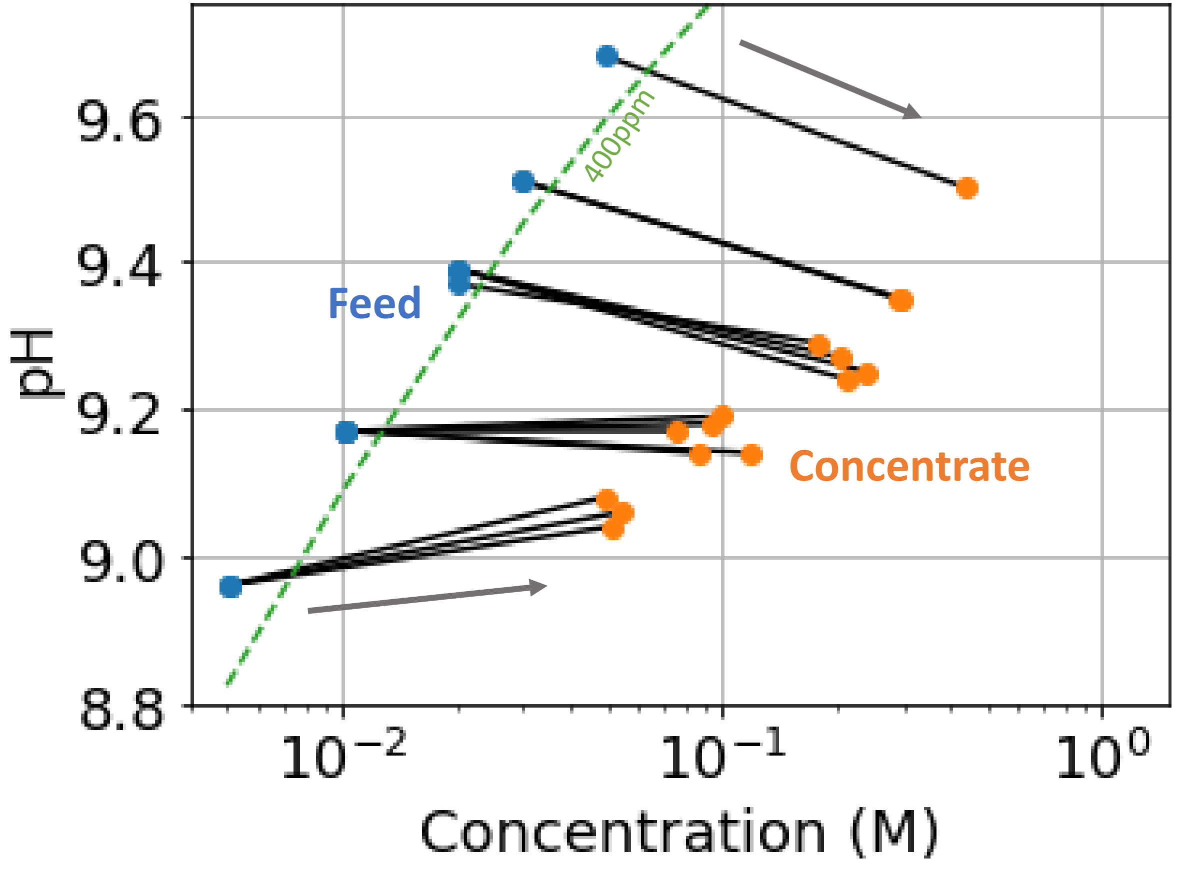
# Measuring the pH shift after concentrating alkalinity

**Experiment set-up:**



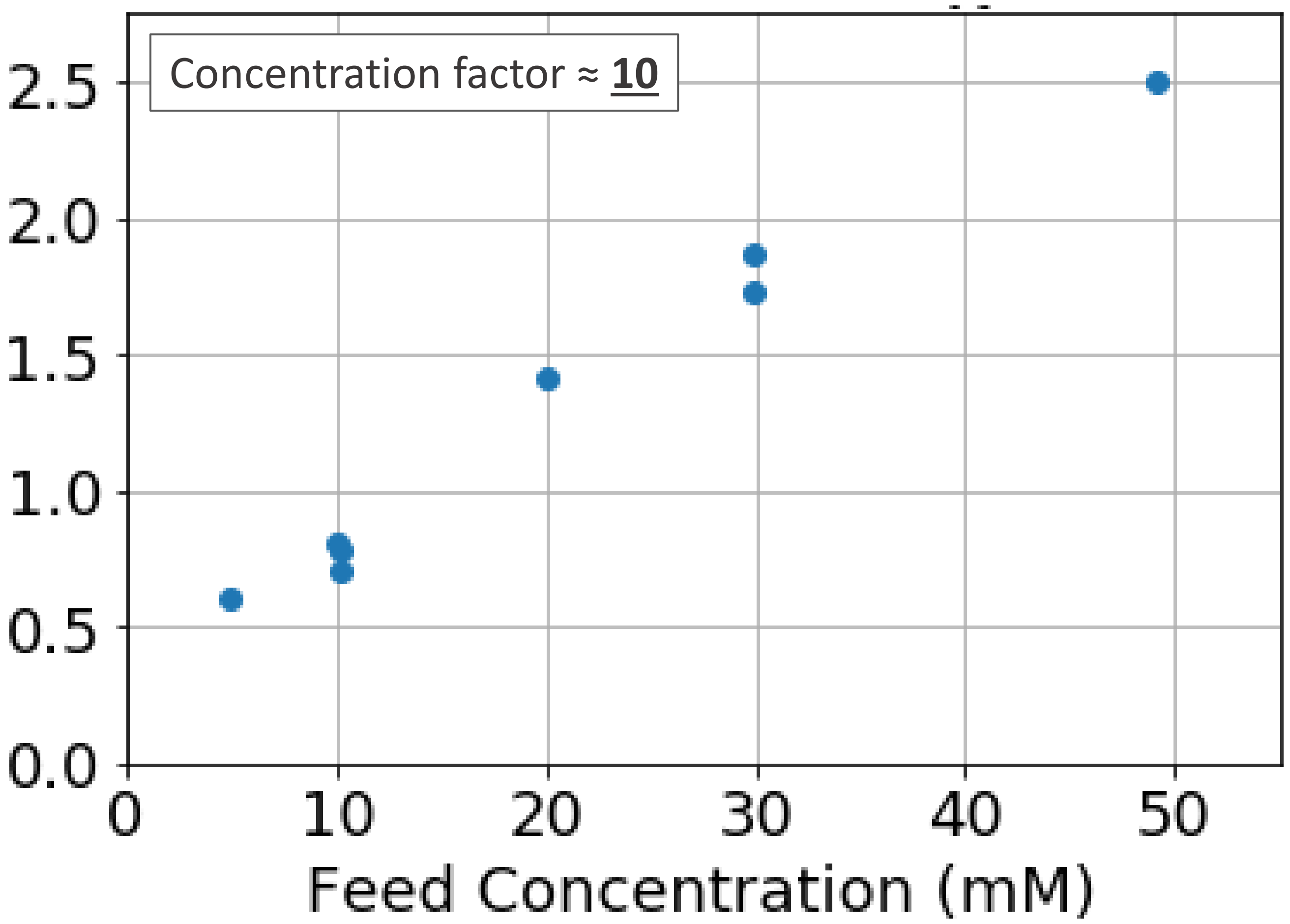
**Feed**: 5, 10, 20, 30, 50 mM $K^+$

**Concentrate by ~10x**



# Higher feed concentrations outgasses more $CO_2$ for the same concentration factor

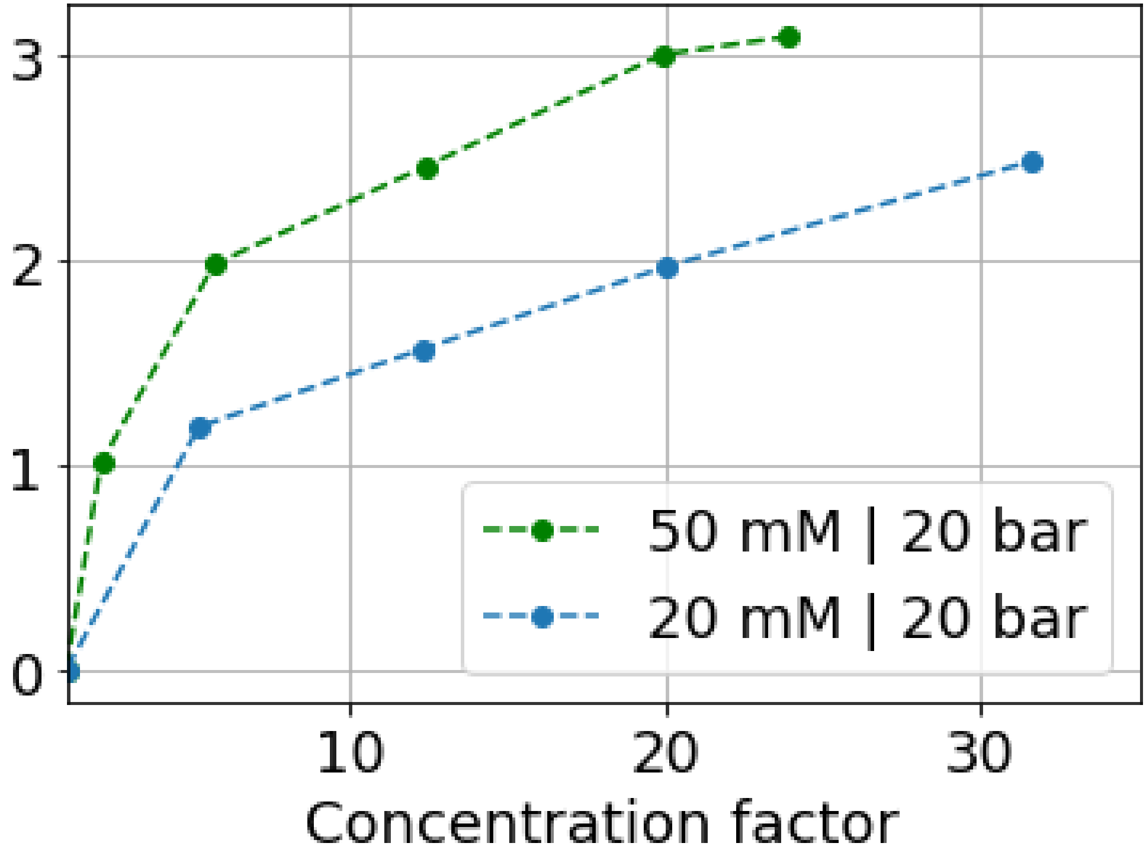
Carbon outgassed for capture (mM)




**Experiment conditions:**
- $K^+$ cation
- Pressure = 20 bar
- Initial volume = 100ml
- Concentration factor ≈ 10

# Higher concentration factor outgasses more $CO_2$

Carbon outgassed for capture (mM)

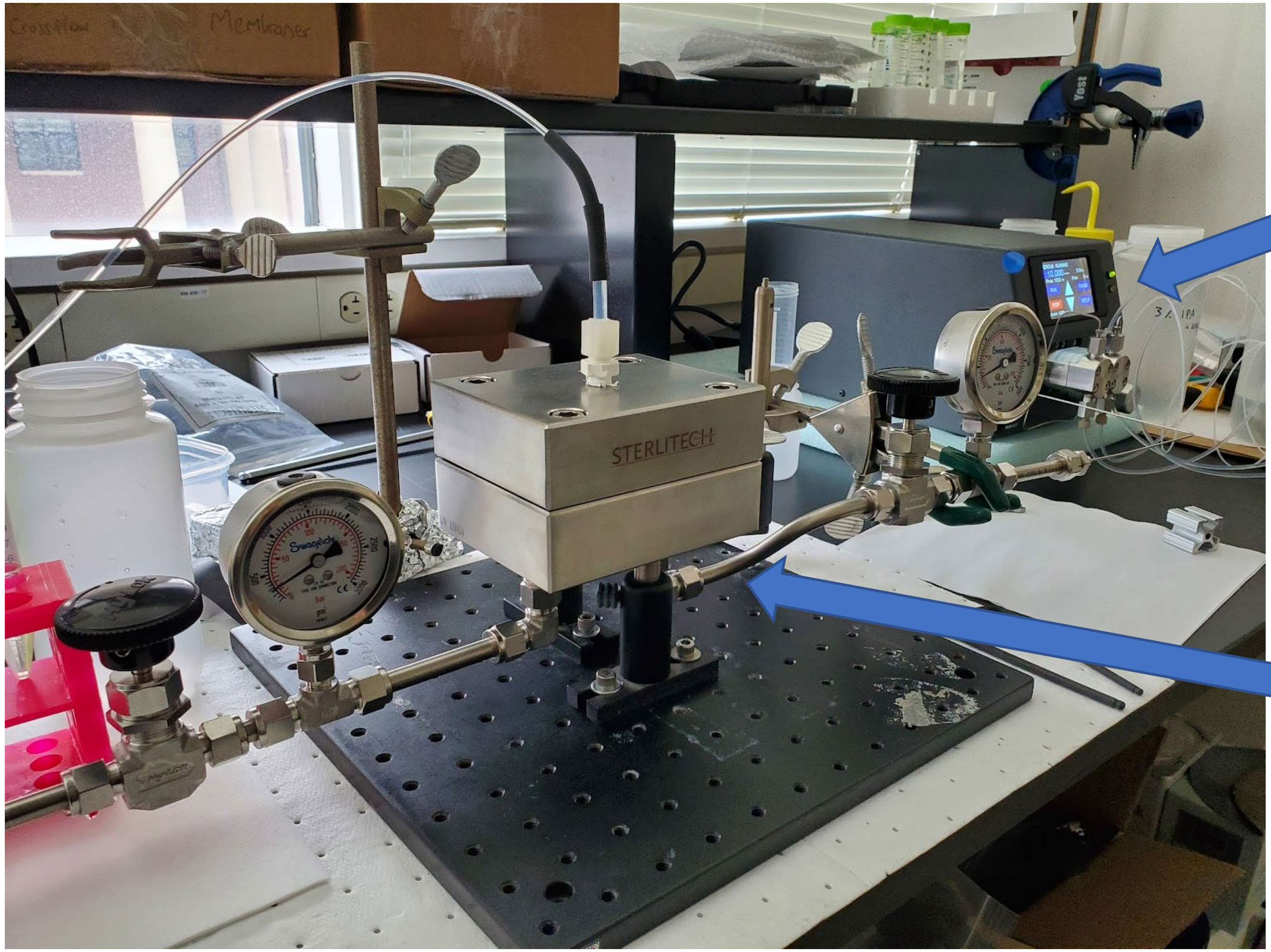



**Experiment conditions:**

- Na+ cation
- Pressure = 20 bar
- Initial volume = 300ml
- Feed concentration 20, 50 mM

# Reverse osmosis crossflow setup operational:

## Sterlitech CF042 cell + ASI high-pressure pump




**ASI high-pressure pump:**
Constant flow condition
Flow rate: 0-40 ml/min
3500 psi max
Continuous digital pressure reading
$P_{max}$ sets shut off pressure for pump

**CF042 Cell specs:**
Membrane area: 42 cm2
Hold-up volume: 17 ml
Typical permeate: 2-20 mL/min
Recommended feed: <2.5 LPM
Pressure limit: 2000 psi

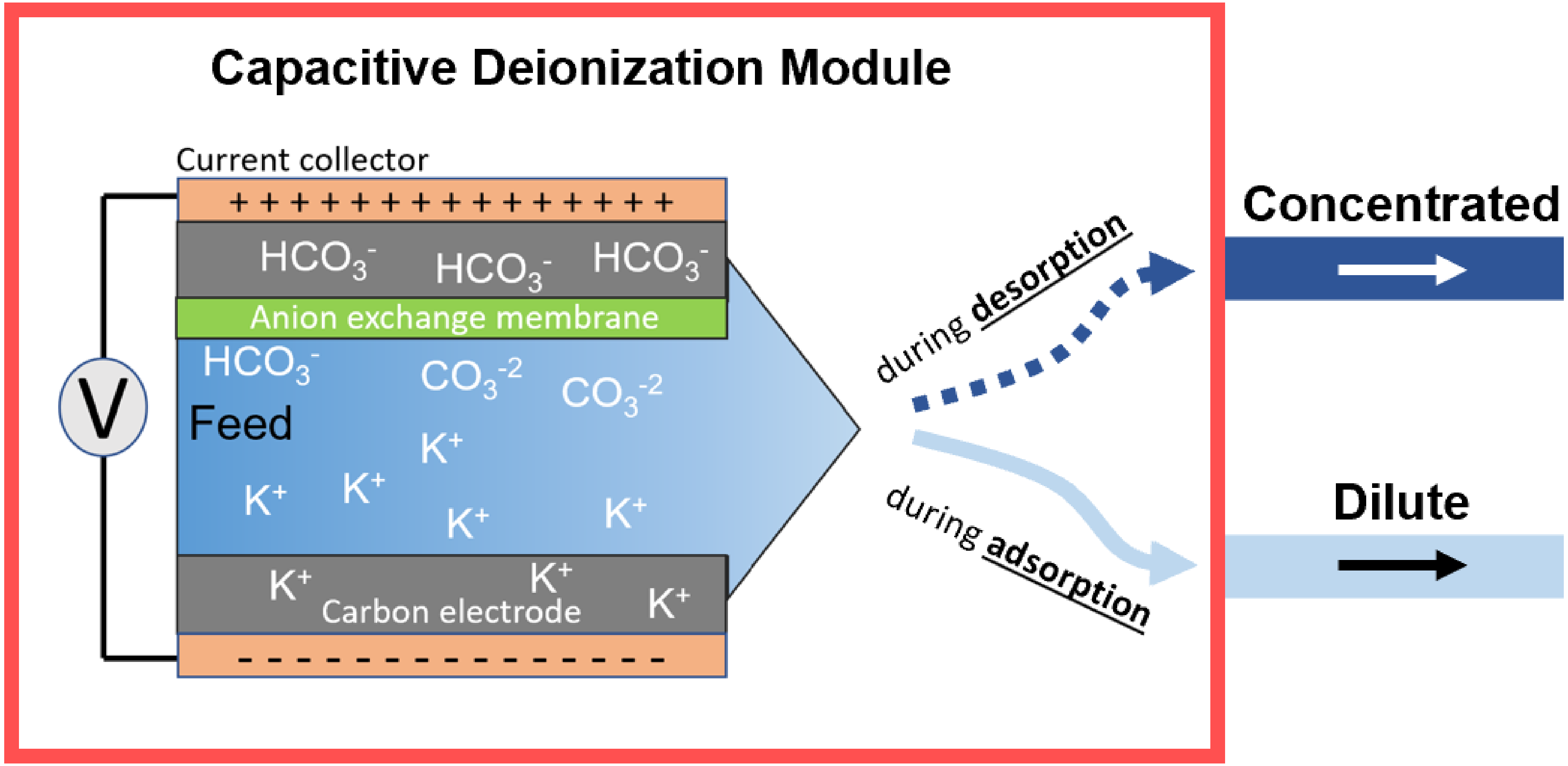
Step 1→2: Concentrating alkalinity

# We explore two implementations of the ACS:

1. **Reverse osmosis** (pressure)

2. **Capacitive deionization** (voltage)

# Using capacitive deionization for the alkalinity concentration swing



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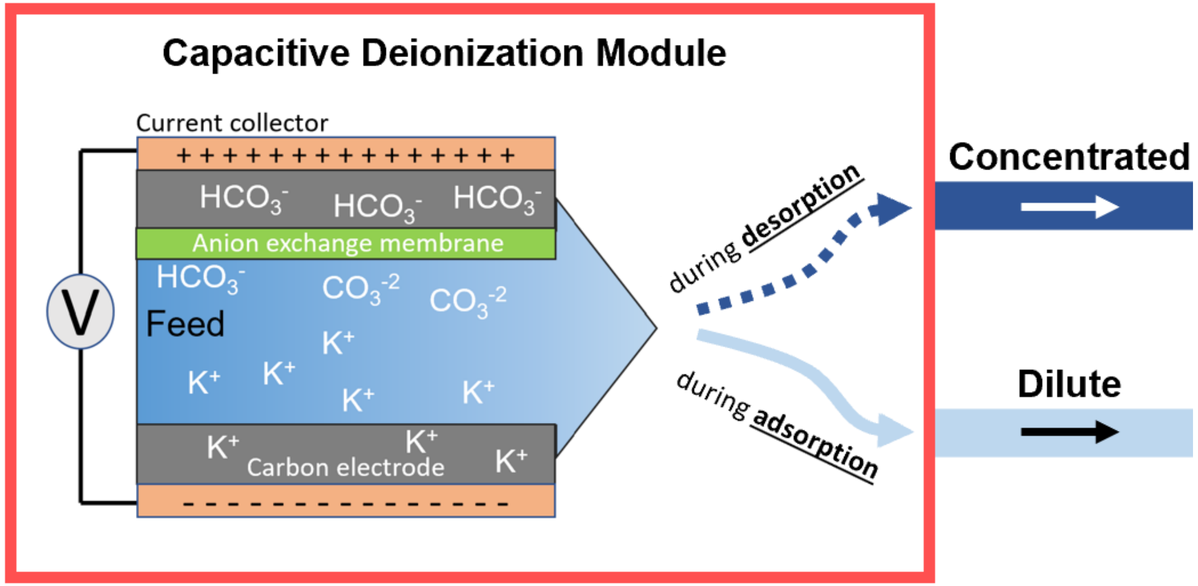



Industrial examples of CDI facilities:

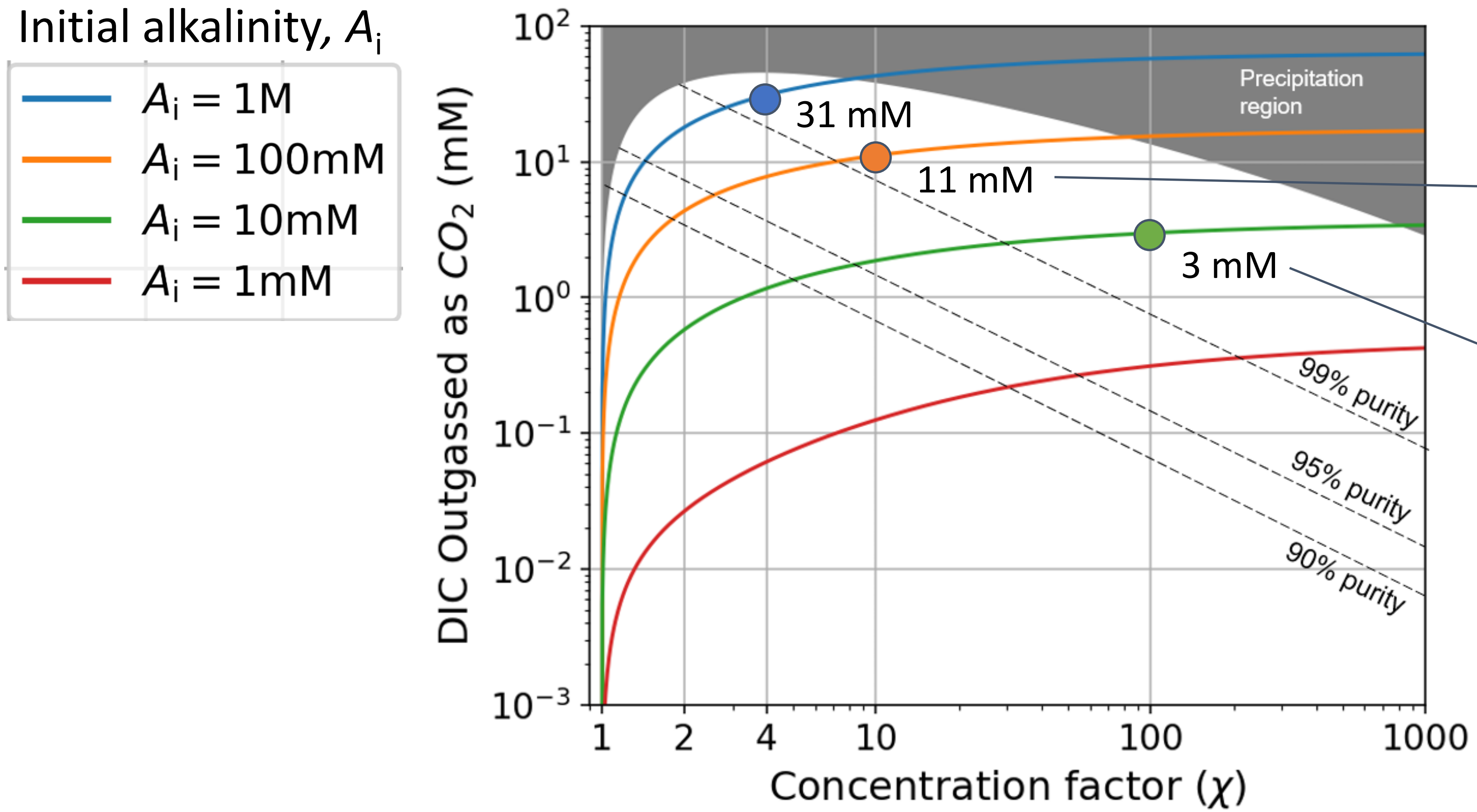
**A) 60,000 m3 / day**

**B) 5,000 m3 /day**



*Suss et al., 2015. "Water desalination via capacitive deionization: what is it and what can we expect from it?"*

# ACS-CDI: Theoretical outgassing and energy




<u>0.1 → 1 M</u>

ACS-CDI: **410-970 kJ/mol**

<u>0.01 → 1 M</u>

ACS-CDI: **170-380 kJ/mol**

Carbon Engineering:

- 360-480 kJ/mol
- 81 mM extraction capacity

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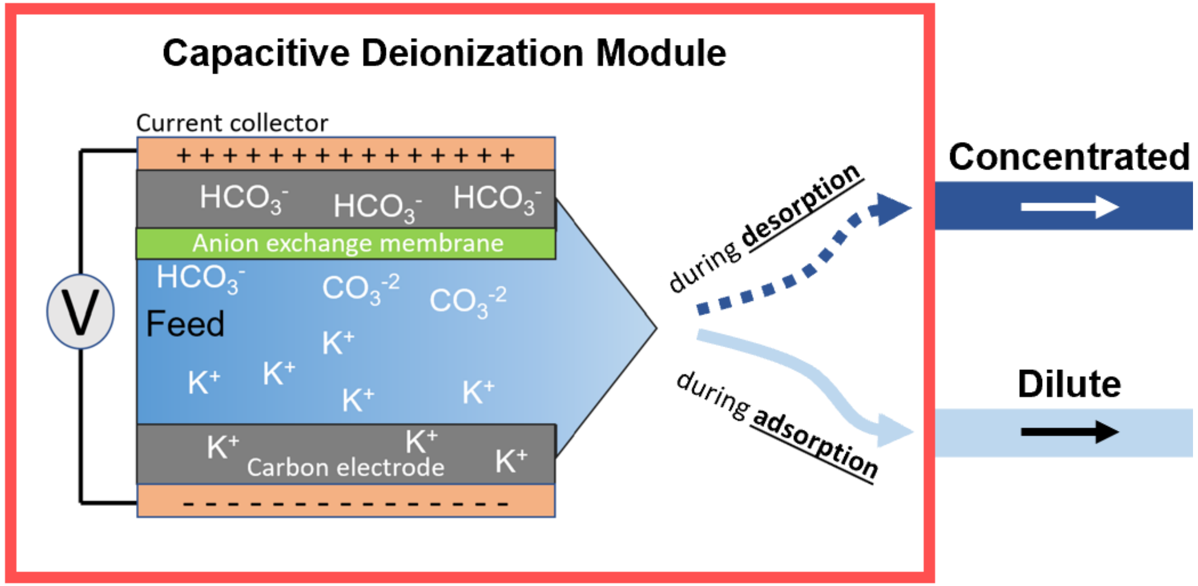
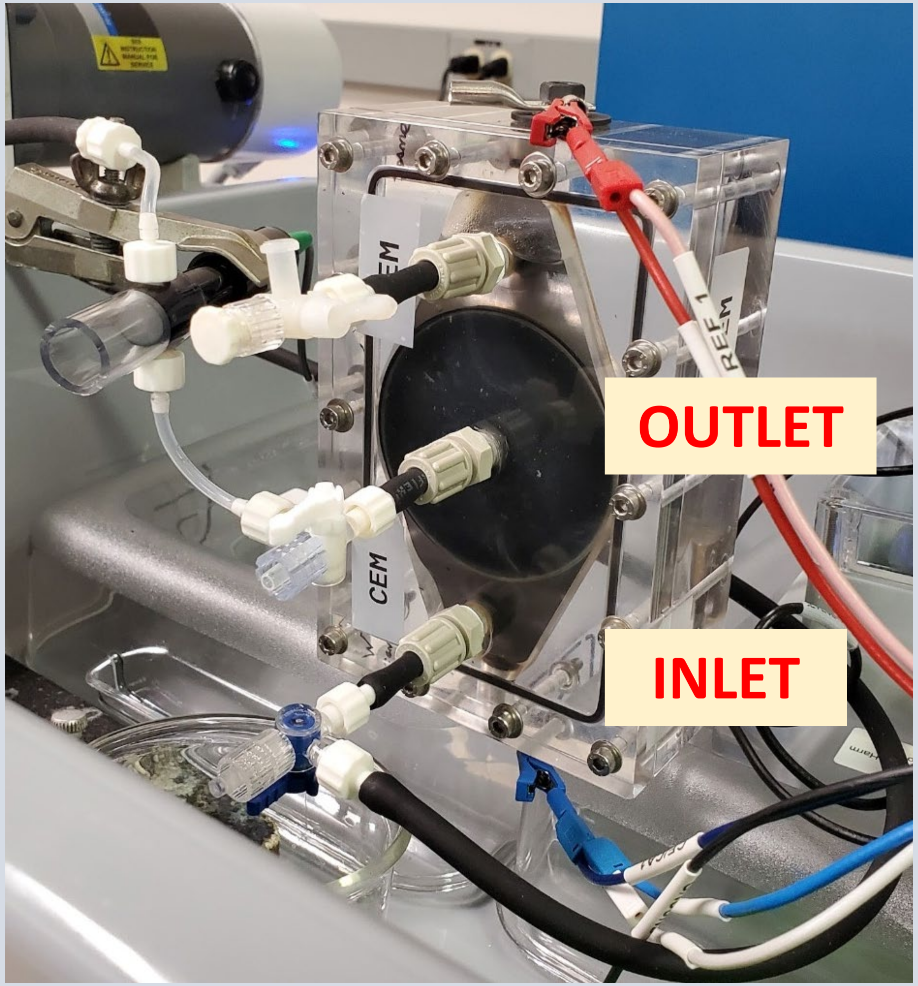
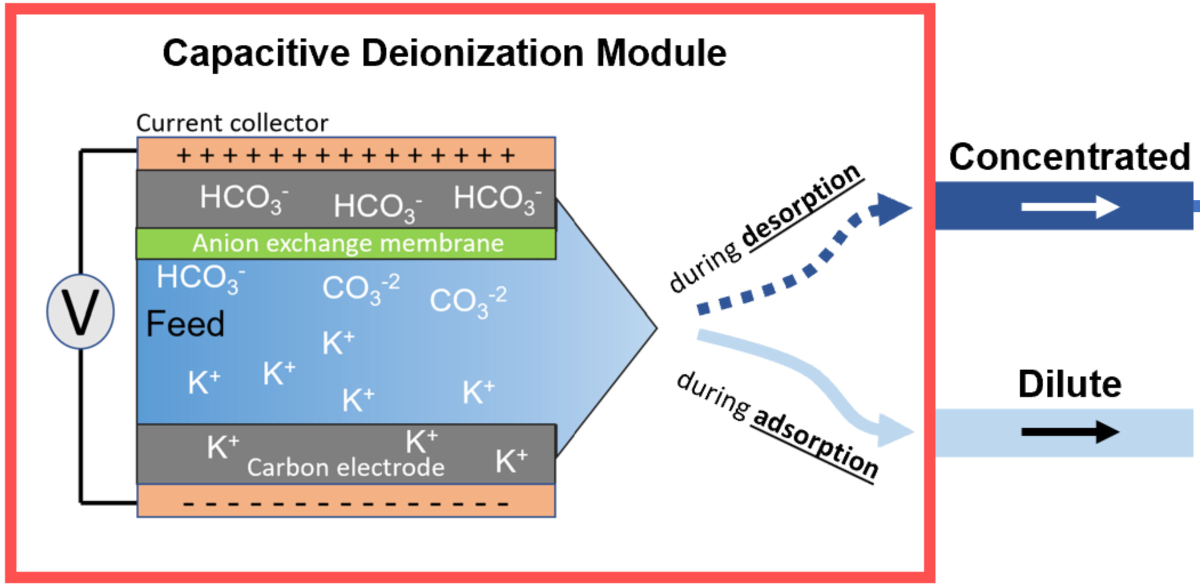


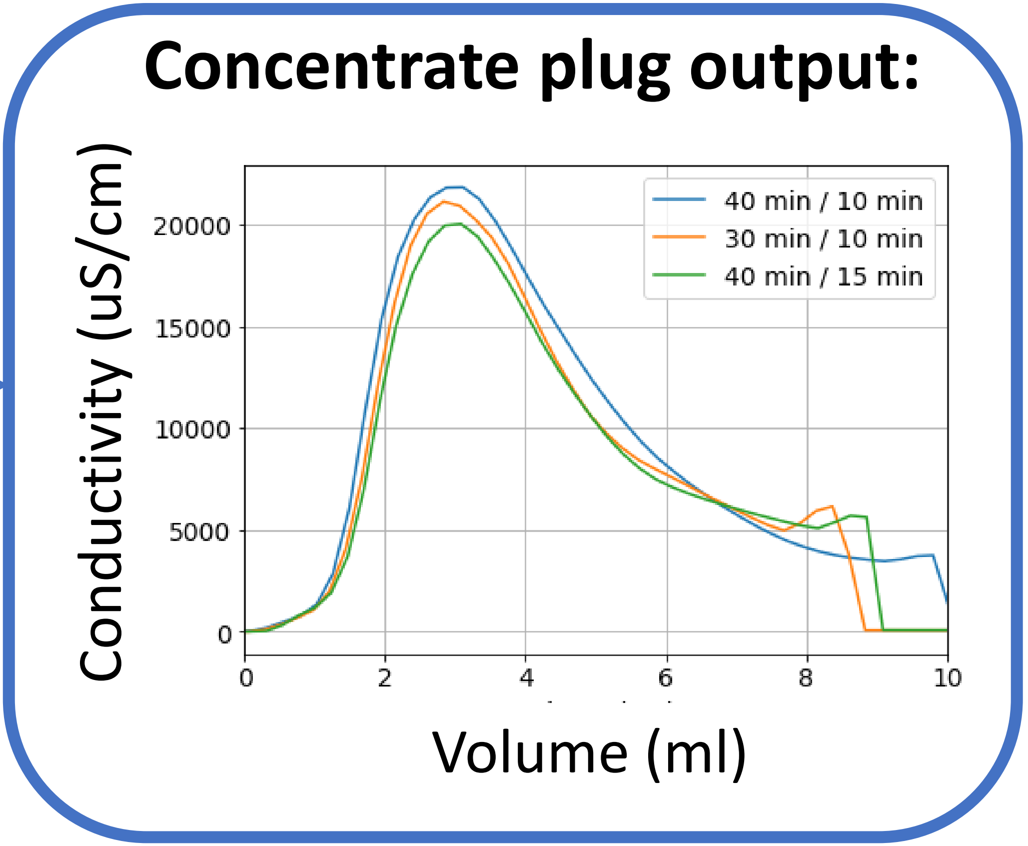

## Lab ACS-CDI cell




*In collaboration with Slawomir Porada and Bert Hamelers at Wetsus Institute, Netherlands*

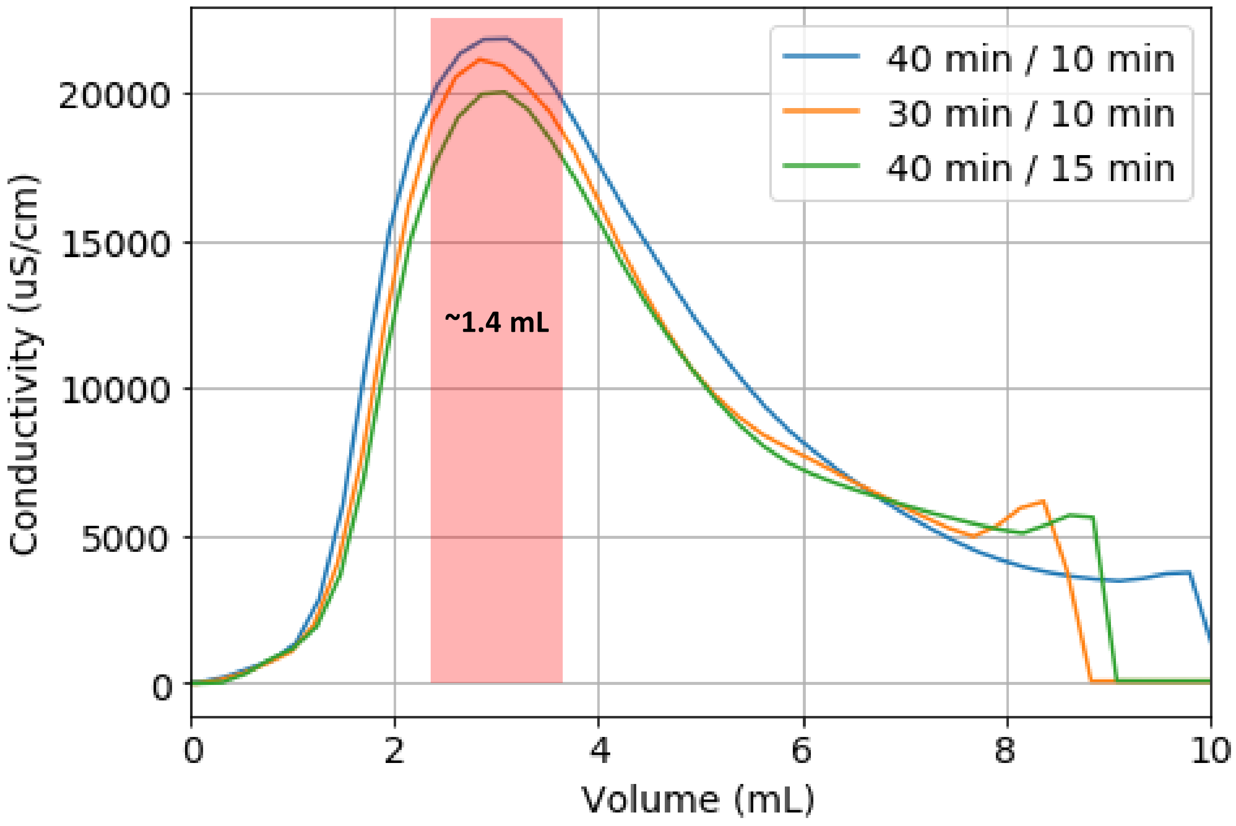
# Using capacitive deionization for the alkalinity concentration swing



# Concentration factor for ~2.5 mM NaDIC initial concentration: **<u>~100x reached</u>**

**Conductivity of concentrate plug**

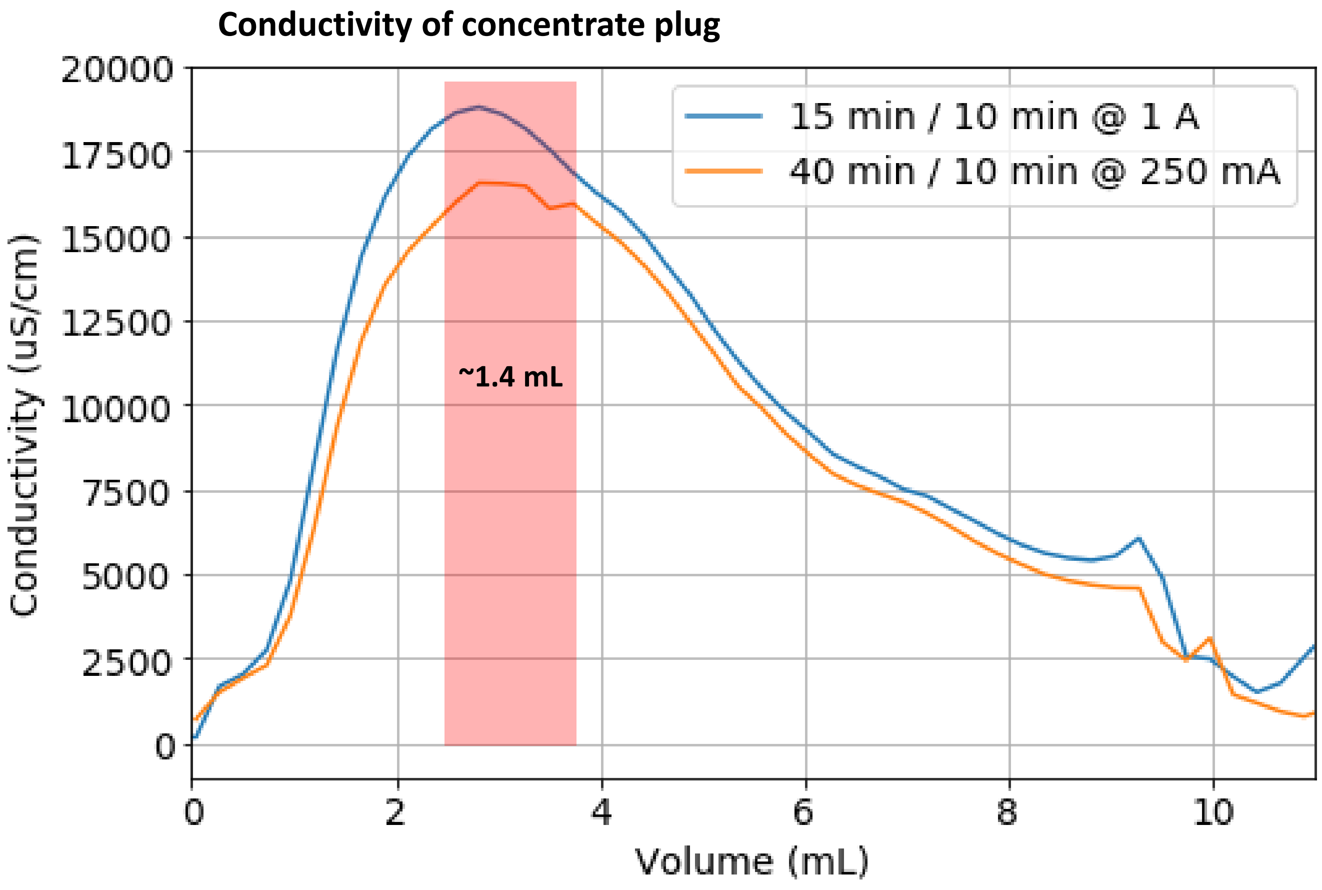



**Results for differing adsorption/desorption times:**

- Peak concentrations reached: **266 - 299 mM**
- Conc. Factor: **108 - 120**
- pCO2 limit: **90.1 - 103 mbar**
- Theoretical CO2 capacity: **0.858 - 0.886 mM**

***Note***: *All measurements are integrated over ~1.4 mL of concentrate*

# Concentration factor for ~25 mM NaDIC initial concentration: <u>**~10x reached**</u>




**Results for differing adsorption/desorption times:**

- Peak concentrations reached: **236 - 267 mM**
- Conc. Factor: **10.0 – 11.4**
- pCO2 limit: **6.59 – 7.65 mbar**
- Theoretical CO2 capacity: **4.87 – 5.04 mM**

**Peak concentration enhancement:**

- Cell architecture modification
- Electrode spacer reduction

***Note**: All measurements are integrated over ~1.4 mL of concentrate*

# Key challenges with the ACS

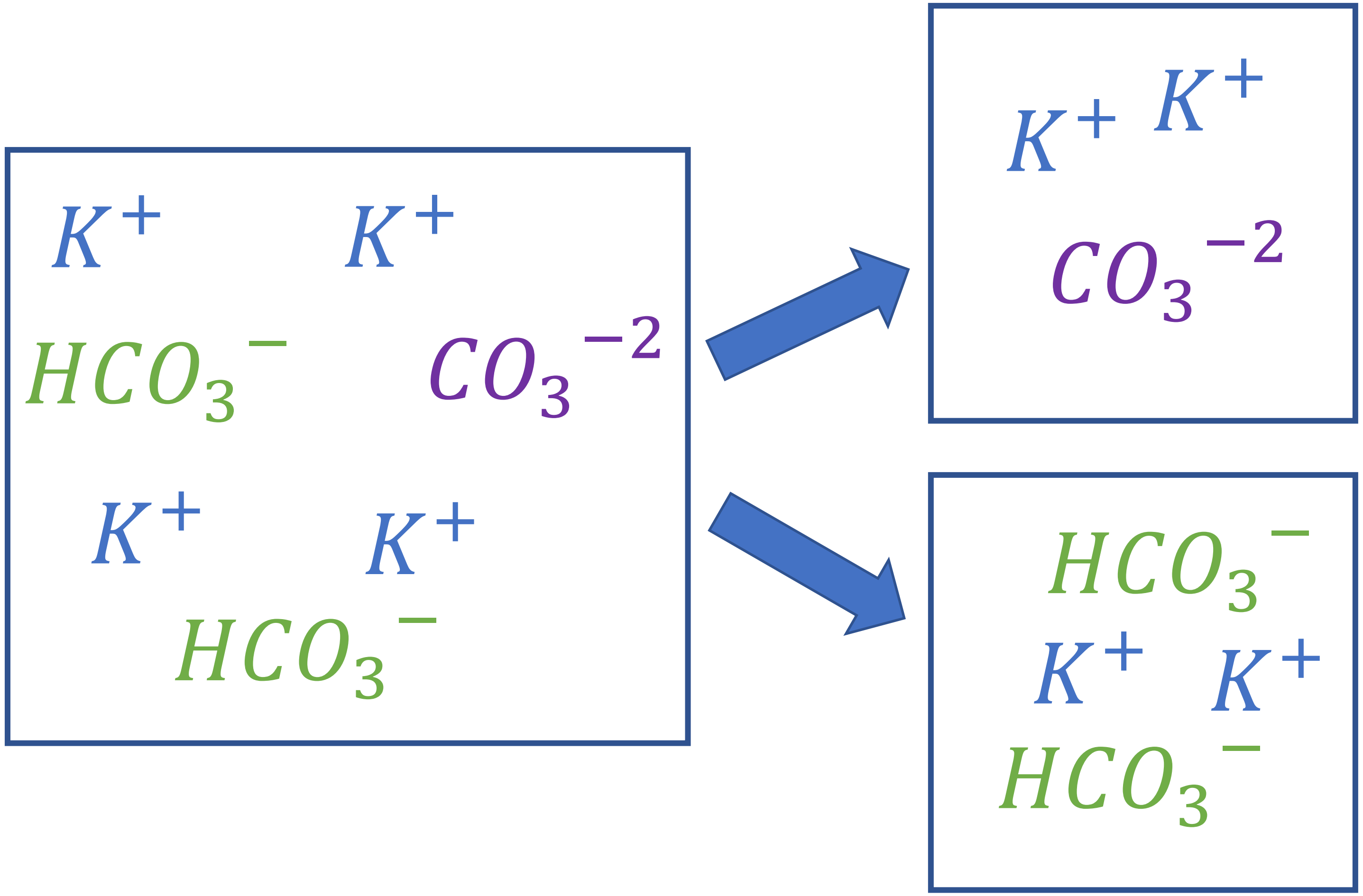
- **Absorption rate**
  - Contacting happens at pH 10-11, which is 30-100x slower than Carbon Engineering's contactor
- **Required water**
  - ~30mM outgassed CO2 is roughly equivalent to a large RO facility water handling
- **Outgassing rate**
  - Partial pressure scales (at least) linearly with concentration factor

# Possible enhancements to the ACS

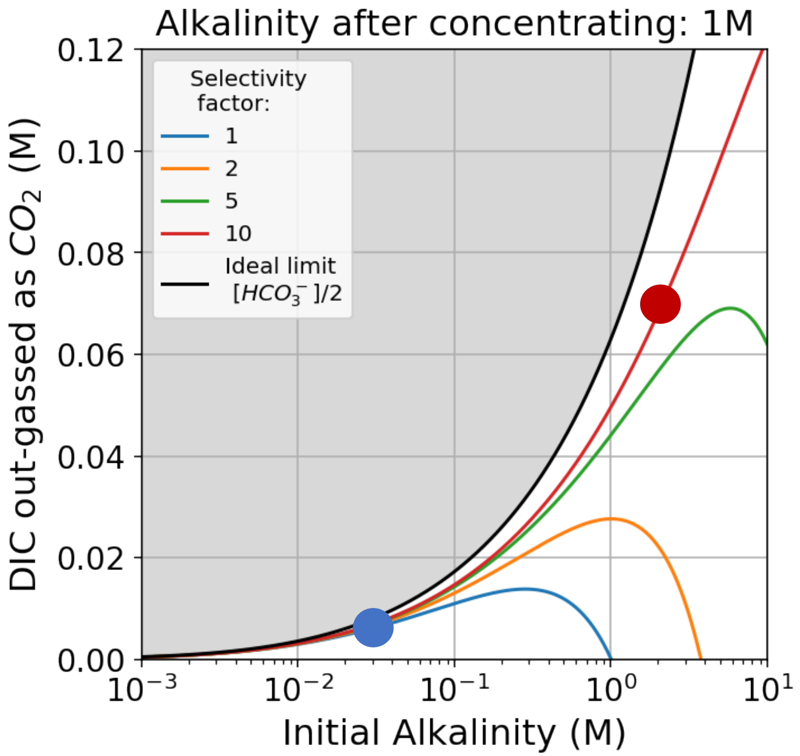
- **Selectivity**: bicarbonate/carbonate separation

- **Solvent enhancement**: Weak acid/base modification

# **Selectivity**: bicarbonate/carbonate separation



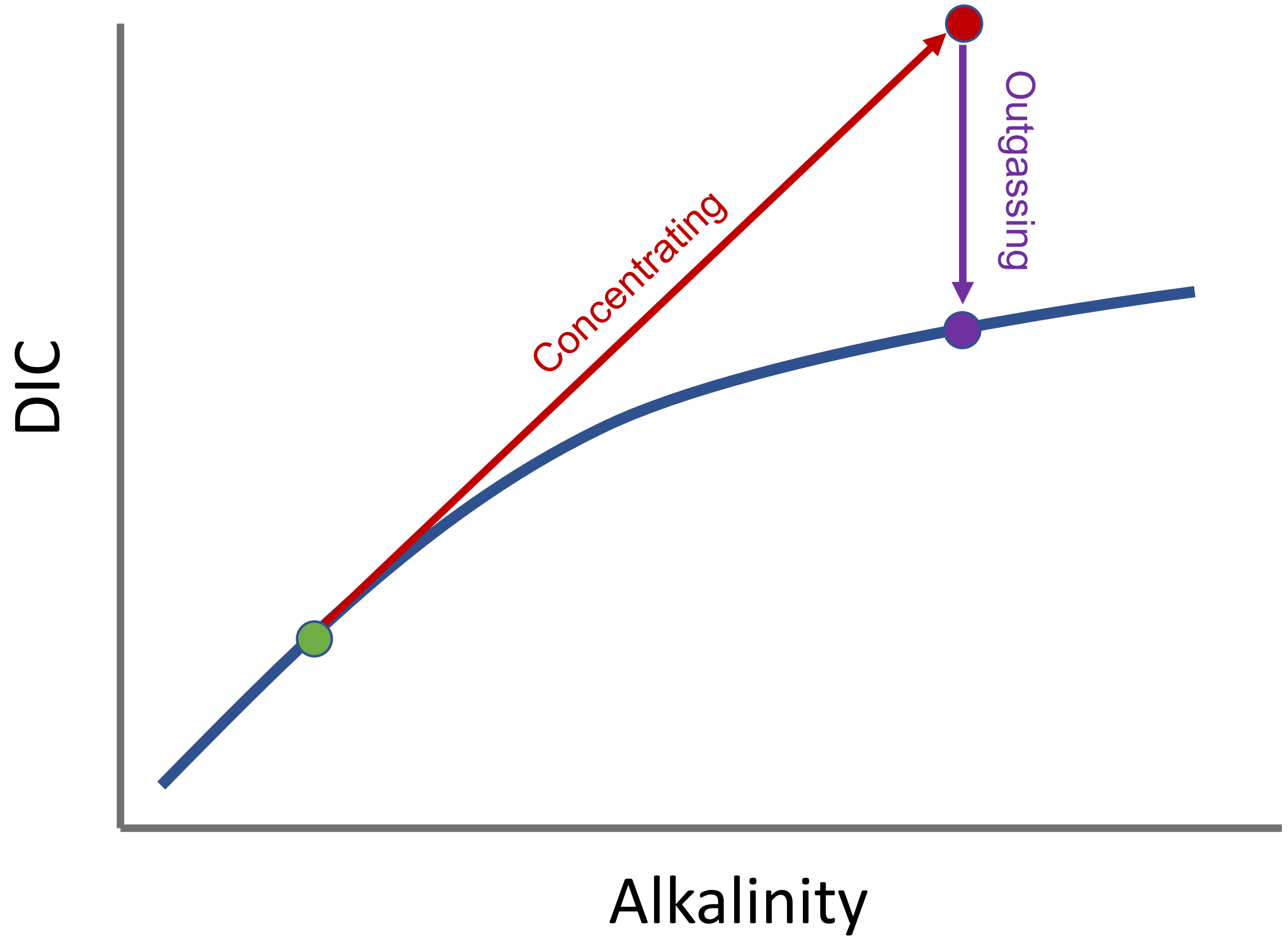

## CDI Analysis




For 250 kJ/mol:

- Selectivity factor 1: 5 mM yield
- Selectivity factor 10: 70 mM yield

# <u>Solvent enhancement</u>: weak acid/ base modification



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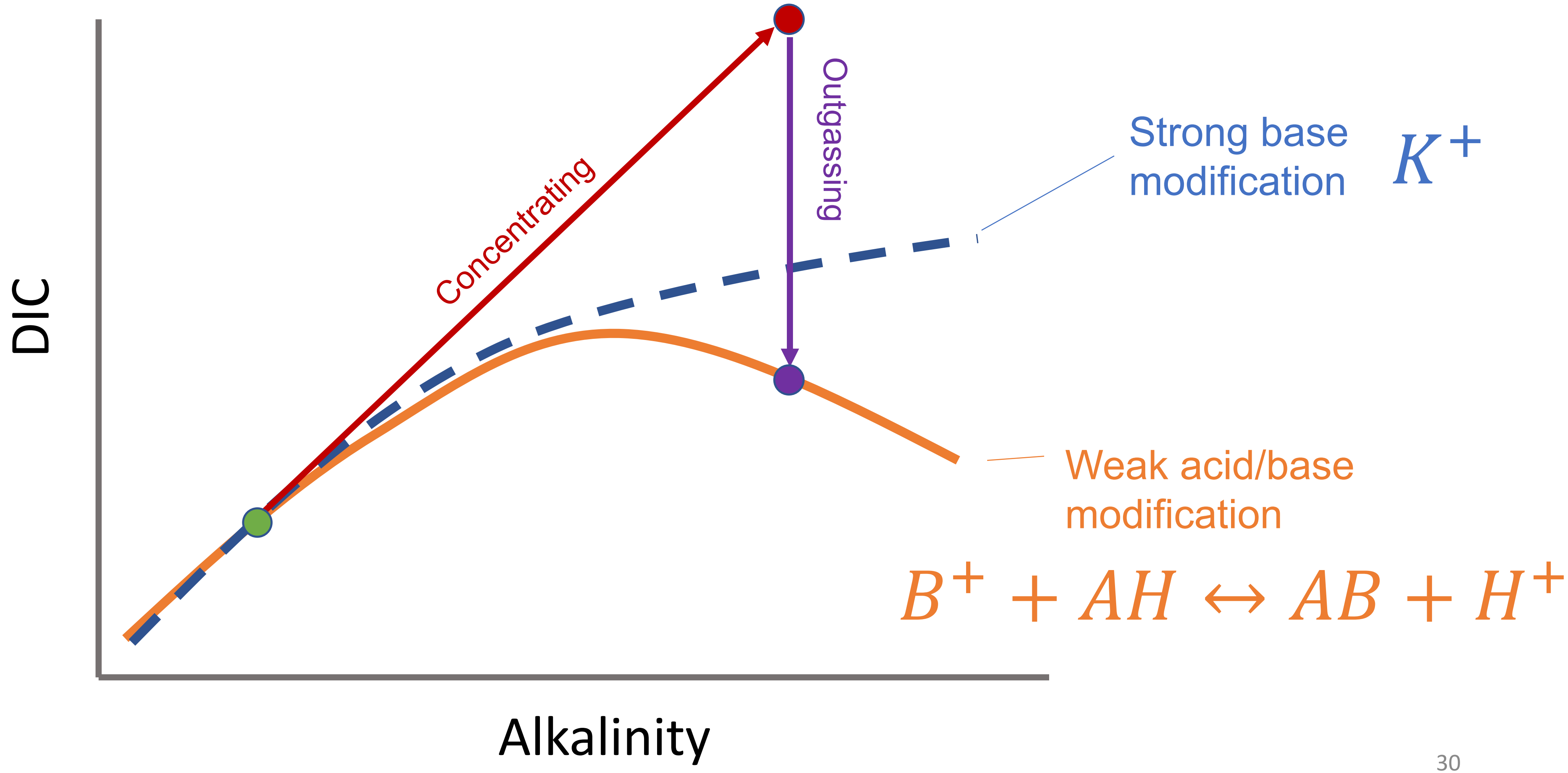

# Main takeaways

**1) ACS-RO and ACS-CDI systems have been assembled and reached our key milestones:**

**10x (RO) and 100x (CDI) concentration factors**

**2) Experimental results qualitatively confirm theory:**

- Higher feed concentration outgasses more $CO_2$
- Higher concentration factor outgasses more $CO_2$

**What next for the alkalinity concentration swing?**

- ACS is highly tunable (feed concentration, concentration factor) allowing for testing of energy-water-rate tradeoffs
  - Energy analysis forthcoming
  - TEA is forthcoming
- Enhancements:
  - Catalysts
  - Bicarbonate/carbonate selectivity
  - Weak acid/base enhancements

# Acknowledgments

Concept paper:

Rinberg*, Bergman*, Schrag, Aziz. **“Alkalinity Concentration Swing for Direct Air Capture of Carbon Dioxide.”** ChemSusChem (2021)

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**Aziz Lab**

- Prof. Mike Aziz (Co-PI)
- Andrew Bergman
- Martin Jin
- Tommy George
- Eric Fell
- Jordan Sosa
- Dawei Xi
- Kiana Amini
- Thomas Cochard

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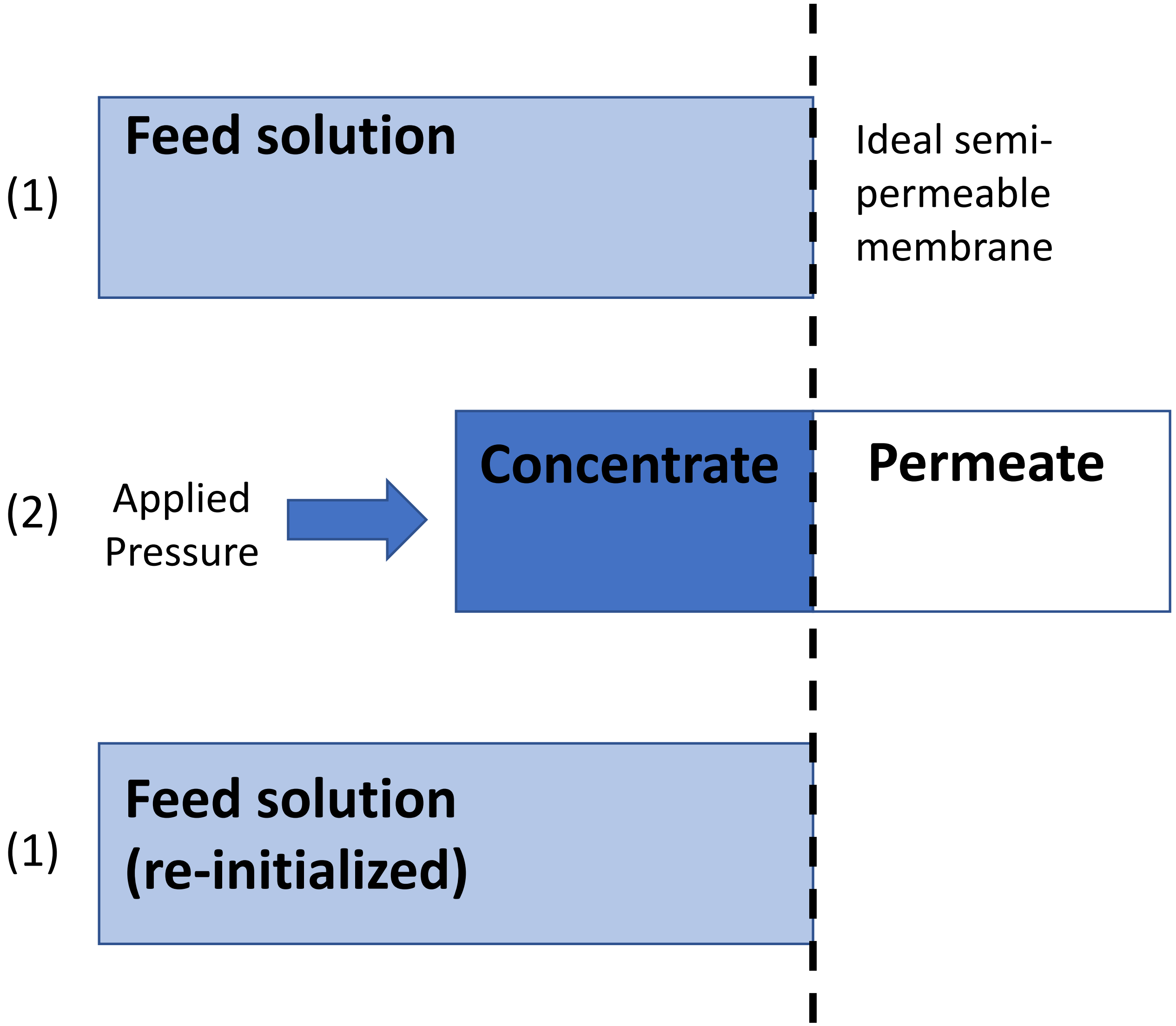
- Harvard Climate Change Solutions Fund

**Prof. Dan Schrag (PI)**

**Collaborators:** CDI cell construction and analysis done in collaboration with Slawomir Porada and Bert Hamelers at Wetsus Institute in the Netherlands

# ADDITIONAL BACKUP SLIDES

# Reverse osmosis cycle: simple model




Van't Hoff Approximation:

**Pressure = RTΔC**



Rinberg*, Bergman*, Schrag, Aziz. **"Alkalinity Concentration Swing for Direct Air Capture of Carbon Dioxide."** ChemSusChem (2021)

# Enhanced charge efficiency and reduced energy use in capacitive deionization by increasing the discharge voltage

T. Kim[a,b], J.E. Dykstra[a,c], S. Porada[a], A. van der Wal[c], J. Yoon[b], P.M. Biesheuvel[a,d,*]

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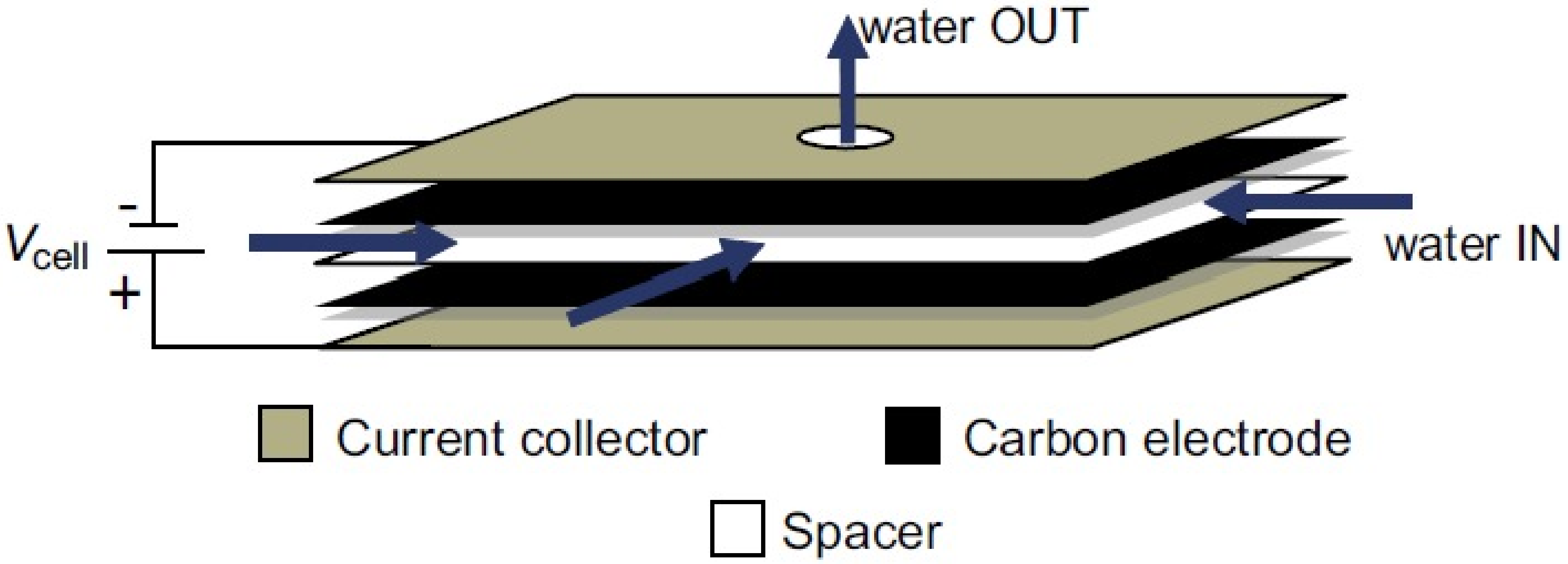
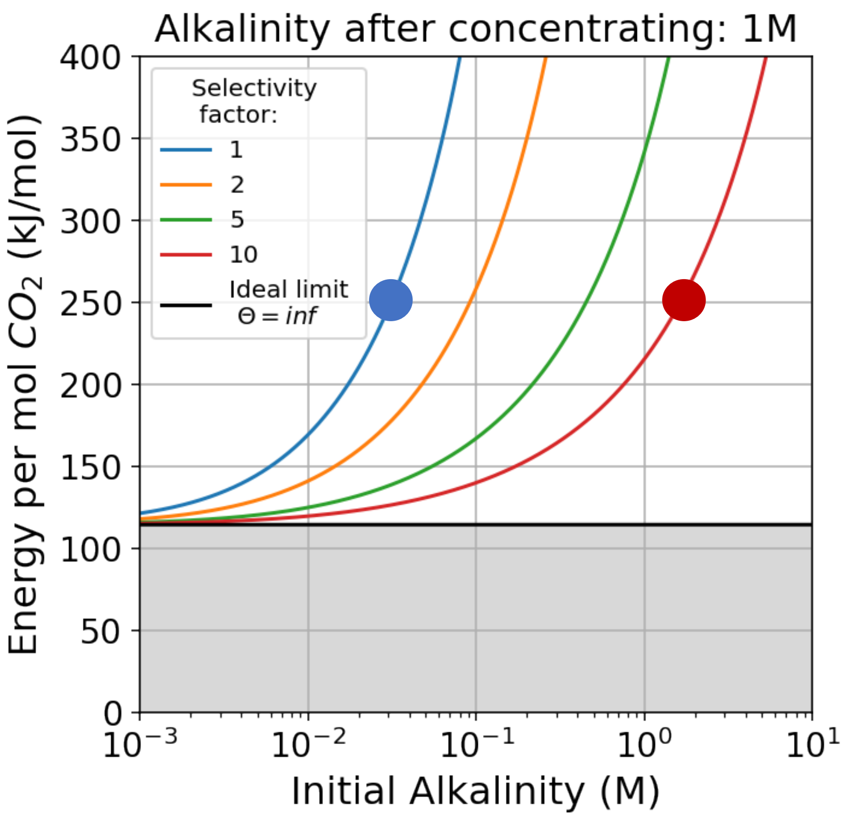
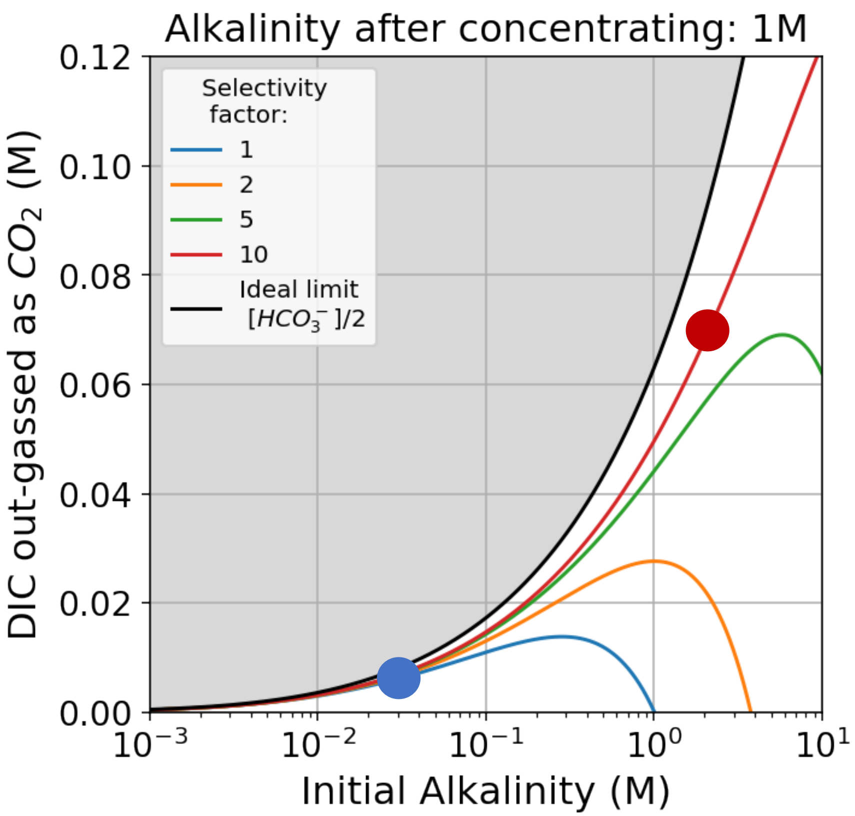
[d] Laboratory of Physical Chemistry and Colloid Science, Wageningen University, Dreijenplein 6, 6703 HB Wageningen, The Netherlands



# ACS-CDI enhancement with bicarbonate selectivity




For 250 kJ/mol:

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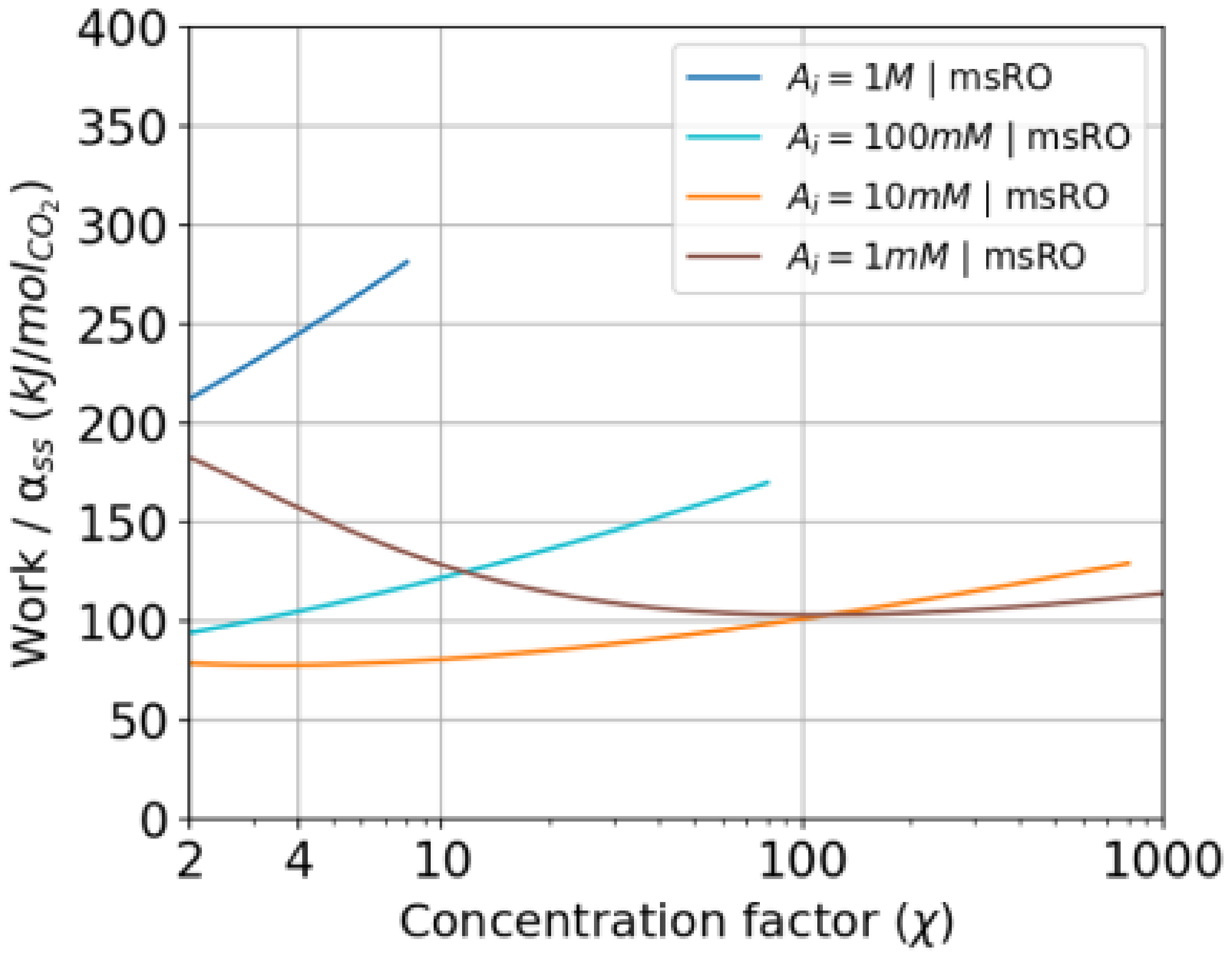
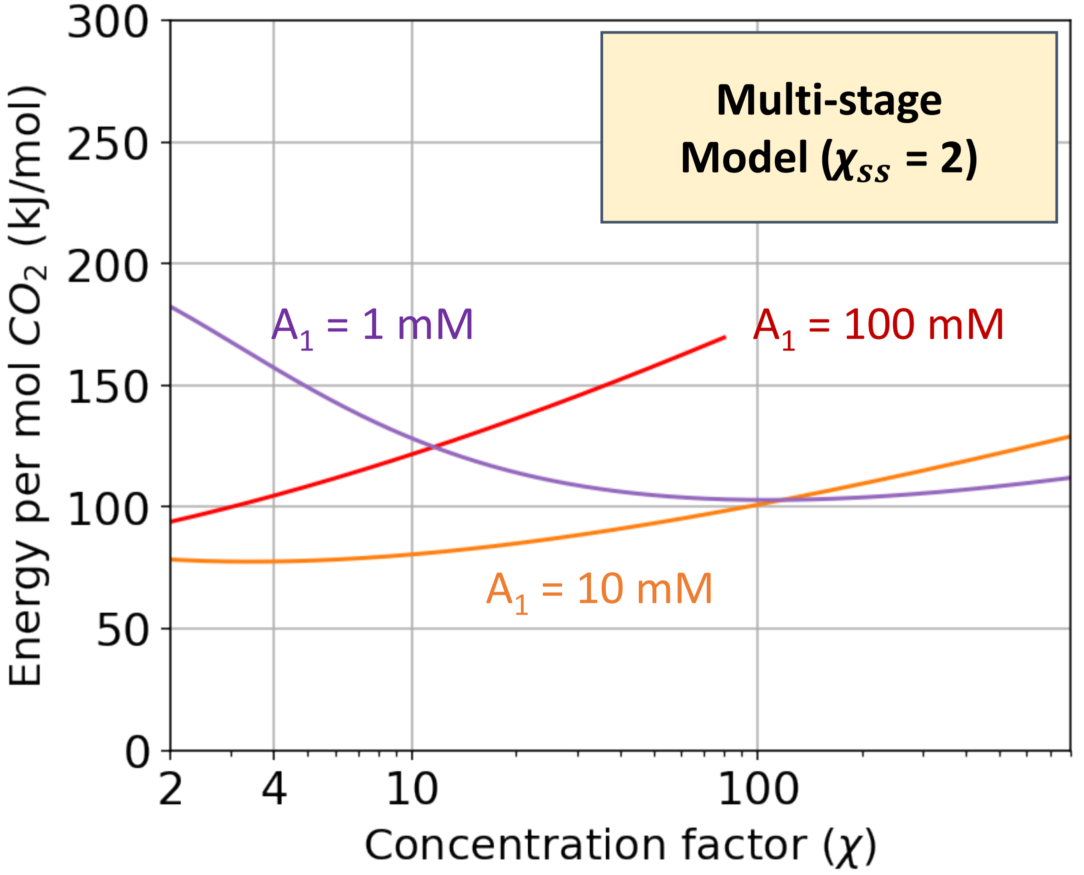
# ACS-RO Theoretical Energy Estimates



# Energy of ACS $CO_2$ capture as a function of concentration factor **and $A_1$**




$p_1$ = 400 ppm | $p_2$ = 400 ppm
Not including vacuum energy

# Aqueous carbonate phase diagram