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 new DAC process based on concentrating the alkalinity of aqueous solution
Dissolved inorganic carbon (DIC) = $[CO_2]_{aq} + [HCO_3^-] + [CO_3^{2-}]$

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

Function of alkalinity (e.g., $[K^+]$)
The alkalinity concentration swing (ACS)

Dissolved inorganic carbon

Alkalinity

$\text{HCO}_3^- - \text{K}^+ \text{K}^+ \text{CO}_3^{2-}$

The alkalinity concentration swing (ACS)

Dissolved inorganic carbon

Absorbing

Alkalinity

Concentrating

Diluting

Outgassing

Bicarbonate disproportionation reaction:

$$2\text{HCO}_3^- \rightarrow \text{CO}_2 + \text{CO}_3^{-2} + \text{H}_2\text{O}$$

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

ACS-RO: theoretical outgassing and energy

Carbon outgassed for capture (mM)

Initial alkalinity:
- $A_i = 1 \text{M}$
- $A_i = 100 \text{mM}$
- $A_i = 10 \text{mM}$
- $A_i = 1 \text{mM}$

**$1 \rightarrow 4 \text{ M}$:**
- Outgassed: $31 \text{ mM}$
- ACS-RO: $350-420 \text{ kJ/mol}$

**$0.1 \rightarrow 1 \text{ M}$:**
- Outgassed: $11 \text{ mM}$
- ACS-RO: $190-220 \text{ kJ/mol}$

**$0.01 \rightarrow 1 \text{ M}$:**
- Outgassed: $3 \text{ mM}$
- ACS-RO: $160-190 \text{ kJ/mol}$

**Carbon Engineering:**
- $360-480 \text{ kJ/mol}$
- $81 \text{ mM}$ extraction capacity

Dead-end cell for preliminary concentration experiments

Cell initialized with feed

High pressure

Concentrate in cell

RO membrane
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.

Experiment conditions:
- K$^+$ cation
- Pressure = 20 bar
- Initial volume = 100ml
- Concentration factor ≈ 10
Higher concentration factor outgasses more CO$_2$

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
- $P_{\text{max}}$ sets shut off pressure for pump

CF042 Cell specs:
- Membrane area: 42 cm$^2$
- Hold-up volume: 17 ml
- Typical permeate: 2-20 mL/min
- Recommended feed: <2.5 LPM
- Pressure limit: 2000 psi
We explore two implementations of the ACS:

1. Reverse osmosis (pressure)

2. Capacitive deionization (voltage)
Using capacitive deionization for the alkalinity concentration swing
Using capacitive deionization for the alkalinity concentration swing

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

Initial alkalinity, $A_i$
- $A_i = 1\, \text{M}$
- $A_i = 100\, \text{mM}$
- $A_i = 10\, \text{mM}$
- $A_i = 1\, \text{mM}$

Carbon Engineering:
- 360-480 kJ/mol
- 81 mM extraction capacity

Using capacitive deionization for the alkalinity concentration swing

In collaboration with Slawomir Porada and Bert Hamelers at Wetsus Institute, Netherlands
Using capacitive deionization for the alkalinity concentration swing

Conductivity (uS/cm)

Volume (ml)

Concentrate plug output:

- 40 min / 10 min
- 30 min / 10 min
- 40 min / 15 min
Concentration factor for ~2.5 mM NaDIC initial concentration: \textbf{\textasciitilde 100x reached}

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

\textbf{Note: All measurements are integrated over \textasciitilde1.4 mL of concentrate}
Concentration factor for ~25 mM NaDIC initial concentration: \textbf{\textasciitilde10x reached}

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 \textasciitilde1.4 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

For 250 kJ/mol:
- Selectivity factor 1: 5 mM yield
- Selectivity factor 10: 70 mM yield
**Solvent enhancement**: weak acid/base modification

![Graph showing DIC vs. Alkalinity](image)
**Solvent enhancement**: weak acid/base modification

\[ B^+ + AH \leftrightarrow AB + H^+ \]
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 CO₂
   • Higher concentration factor outgasses more CO₂

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
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Concept paper:

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ADDITIONAL BACKUP SLIDES
Reverse osmosis cycle: simple model

Van’t Hoff Approximation:

\[ \text{Pressure} = RT\Delta C \]

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

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ACS-CDI enhancement with bicarbonate selectivity

For 250 kJ/mol:
- Selectivity factor 1: 5 mM yield
- Selectivity factor 10: 70 mM yield
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

DIC (M) vs. Alkalinity (M)

- Region 1: Concentrating
- Region 2: Outgassing
- Region 3: Diluting

Phases:
- CO$_3^{2-}$
- HCO$_3^-$

Pressure (P$_{CO2}$) = 0.4 mbar