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 GtCO₂/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^-] + 2[CO_3^{2-}]

~420ppm CO_2

\[
CO_2 (aq) + H_2O \leftrightarrow HCO_3^- + H^+ \leftrightarrow CO_3^{2-} + 2H^+
\]

dissolved carbon dioxide (0.014 mM)

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

Dissolved inorganic carbon

Alkalinity

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

Dissolved inorganic carbon

Absorbing

Concentrating

Outgassing

Diluting

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

\[ 2\text{HCO}_3^- \rightarrow \text{CO}_2 + \text{CO}_3^{2-} + \text{H}_2\text{O} \]
ACS full system schematic

Rinberg*, Bergman*, Schrag, Aziz, “Alkalinity Concentration Swing for Direct Air Capture of Carbon Dioxide.” ChemSusChem (2021)
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:
- $A_i = 1$ M
- $A_i = 100$ mM
- $A_i = 10$ mM
- $A_i = 1$ mM

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

- 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
Dead-end cell for preliminary concentration experiments

Cell initialized with feed

High pressure

Concentrate in cell

RO membrane

Permeate

Outgassed CO₂

Permeate
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 $\approx$ 10

Carbon outgassed for capture (mM)
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
  - \( P_{max} \) 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, $A_i$

- $A_i = 1$ M
- $A_i = 100$ mM
- $A_i = 10$ mM
- $A_i = 1$ 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 (μS/cm)
Volume (ml)

**Concentrate plug output:**

![Graph showing conductivity and volume changes with different desalination times.](image)

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

Results for differing adsorption/desorption times:

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

Note: All measurements are integrated over \textbf{\sim 1.4 mL of concentrate}
Concentration factor for ~25 mM NaDIC initial concentration: ~10x 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 ~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

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 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
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Concept paper:
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ADDITIONAL BACKUP SLIDES
Reverse osmosis cycle: simple model

Van’t Hoff Approximation:

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

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

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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 CO₂ capture as a function of concentration factor and A₁

$p_1 = 400 \text{ ppm} \mid p_2 = 400 \text{ ppm}$

Not including vacuum energy
Aqueous carbonate phase diagram