# Experimental Demonstration of Alkalinity Concentration Swing for Direct Air Capture of Carbon Dioxide

# primary project goal

Harvard University is conducting experimental verification of a novel approach for direct air capture (DAC) of carbon dioxide (CO<sub>2</sub>) that employs an alkalinity concentration swing (ACS) process. ACS involves concentrating an aqueous alkaline solution (that has equilibrated with air) using commercially available technologies such as reverse osmosis (RO) or capacitive deionization (CDI). The concentrated solution has a higher partial pressure of CO<sub>2</sub> relative to the initial solution, allowing the CO<sub>2</sub> to be separated and stored.

# technical goals

- Adapt the design of RO and CDI from their traditional desalination uses and tune each for a specific target concentration factor (10-times for RO; 100-times for CDI) necessary to extract CO<sub>2</sub> from alkaline solution.
- Assemble a calibrated system to measure CO<sub>2</sub> extracted from solution and build a subsystem to extract CO<sub>2</sub> from concentrated solution using either a vacuum on a fluid reservoir and/or using gas permeable membrane technology.
- Use CO<sub>2</sub> measurement and extraction systems to test the solution's equilibrium and kinetic properties key to the ACS, including how dilution and re-equilibration with air proceed.
- Demonstrate system integration and energy quantification coupled to the ability to extract CO<sub>2</sub> from solution concentrated by RO or CDI and measure the energy necessary to operate the process per quantity of CO<sub>2</sub> captured.
- Develop an understanding of breakdown pathways and confirm the revolutionary stability of the new solvent using various laboratory techniques.

# technical content

The concentration of dissolved inorganic carbon (DIC)-the sum of carbonate ion, bicarbonate ion, and dissolved CO<sub>2</sub>—in equilibrium with air (pCO<sub>2</sub> ≈ 415 parts per million [ppm]) depends on the alkalinity of a solution (i.e., the charge difference between the sum of the conservative cations and anions in solution). As the alkalinity of a solution increases, the amount of DIC, when equilibrated with air, increases, but at a decreasing rate. This is due to the transition from bicarbonate as the dominant species of DIC (at an intermediate pH range from 6.5-10) to carbonate ion as pH increases. At higher alkalinity and higher pH, the charge balance required is now accommodated primarily by carbonate ions, which are divalent. Consider any basic solution in equilibrium with air-if pure water is removed from this solution in a closed system with respect to the dissolved components (including CO<sub>2</sub>), both the DIC and the alkalinity increase in proportion to their relative concentrations in the solution, while the partial pressure of CO<sub>2</sub> steadily increases, due to the change in speciation of carbon from bicarbonate to carbonate. This creates an opportunity for collection of CO<sub>2</sub> in concentrated form. The solution can be recycled simply by recombining the concentrated solution with the freshwater produced from the RO or CDI modules and then allowing it to re-

# program area:

Carbon Dioxide Removal

ending scale: Laboratory Scale

application: Direct Air Capture

key technology: Solvents

project focus:

Alkaline Concentration Swing Process for DAC

participant: Harvard University

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predecessor projects: N/A

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equilibrate with air, returning the system to the initial point. The cycle is illustrated in Figure 1, which shows the first two steps (concentration and outgassing) of the ACS.



Figure 1. The ACS cycle (concentrating and outgassing steps).

Figure 1 plots a representative example of a solution at 0.01 M alkalinity (K+), equilibrated at  $pCO_2$  of 400 ppm, concentrated by a factor of 100 to 1 M alkalinity. At these values, the solution will outgas 3 mM of  $CO_2$  with respect to the feed. In Figure 1, the blue line plots the relationship between DIC concentration at a fixed partial pressure of  $CO_2$  (400 ppm) as a function of alkalinity. The red arrow indicates the concentration step of the ACS and plots the trajectory in DIC and alkalinity space if a solution that was equilibrated at 0.01 M alkalinity (green point) was concentrated by a factor of 100 times to an alkalinity of 1 M. In the concentrated state (red point), the solution has an excess DIC to the amount of alkalinity in solution. When exposed to a pressure of 400 ppm, the purple arrow indicates the amount of  $CO_2$  that would outgas as the system reaches a new equilibrium at high alkalinity. This figure does not show the remaining step of the ACS, dilution and atmospheric  $CO_2$  re-equilibration, which would return the system to the initial point.

This basic approach will work with any strong base. Potassium hydroxide solutions are the solvent of choice due to the very high solubility of potassium bicarbonate. Sodium bicarbonate is less soluble, and the concentration step may drive precipitation of solids, which would complicate the process; calcium carbonate is even less soluble. There are multiple tradeoffs to consider in terms of what concentrations to use for optimization of the ACS process. Starting with more dilute solutions (e.g., 0.01 M), and then concentrating by a factor of 100, can produce a higher CO<sub>2</sub> outgassing pressure from the concentrated solution, but requires more energy for the concentration step and a larger initial feed solution volume. On the other hand, starting with a more concentrated initial solution (e.g., 0.6 M) can result in a significantly lower ACS energy requirement and, at this higher initial alkalinity, ingassing kinetics (i.e., re-equilibration with air following dilution) are also significantly faster, based on estimates using the literature.

It is difficult to make detailed calculations of the energy demand of DAC without experimental demonstration of the full cycle as is being performed in this project. However, using standard numbers for energy use in RO desalination plants and at similar concentration ranges, a rough estimate of 1.7 megawatt-hours (MWh) of electricity per tonne of CO<sub>2</sub> was obtained, which suggests there is potential for improvement on the 2.28-MWh minimum energy requirement in published estimates of solvent-based DAC energy requirements. Another important advantage of the ACS approach to DAC is that, because it makes use of existing technologies for water purification and desalination that are widely deployed at commercial scale around the world (such as RO), the capital costs of this approach to DAC are likely to be extremely low. High capital approaches to DAC require steady power supply and continuous operation to reduce costs; ACS has

the potential to harness very inexpensive but intermittent energy sources (such as wind) that would be impossible if capital costs for the system were high.

This project's approach to experimental demonstration of ACS is to first test each step of the system independently before integrating them into a full cycle. The process has been divided into three subsystems (shown in Figure 2).

- 1. Concentration of an alkaline solution.
- 2. Carbon dioxide extraction.
- 3. Dilution and re-equilibration with air.

For the concentration step, which is at the heart of the ACS process, the project team is conducting experiments on two parallel approaches. First, to use a laboratory-scale RO desalination system; second, to use a CDI system that has advantages at lower concentration ranges. One experimental range of concentrations for the ACS is being used in both systems to allow for direct comparisons. Two approaches for CO<sub>2</sub> extraction—one applying a vacuum on a fluid reservoir and another making use of gas permeable membrane technology are also being evaluated.



Figure 2. System schematic for ACS implementation. (A) Flow diagram indicating the three steps of the ACS: (1) concentration; (2) CO<sub>2</sub> extraction; (3) dilution and re-equilibration with air.

#### **Concentration Step Using RO**

RO is a membrane-based separation process where pressure is applied against a solvent-filled solution, overcoming the solution's osmotic pressure, to create a concentrated and purified stream. RO technology has a wide range of applications, from wastewater treatment and home water purification to seawater desalination. Desalination plants are designed to produce a stream of freshwater from an input feed of about 0.6 M of sodium chloride (NaCl)-equivalent salt (i.e., seawater), yielding a brine of roughly double the original salinity. This exact process can be used to demonstrate the carbon capture approach of the ACS, but different membranes need to be tested, in particular with respect to rejection of DIC and the alkalinity carrier (K+), as well as water permeability-both factors that contribute to the maximum reachable concentration factor. Unlike in traditional desalination processes, higher permeability may be tolerated since minimizing the salinity of the permeate stream is not a necessary optimization goal for the ACS. Initially, a range of commercially available polyamide thin-film composite membranes and cellulose acetate membranes are being tested, deploying different membrane performance parameters testing salt rejection between 95-99% and permeabilities between 28.9–68 L/m<sup>2</sup>/h, over a range of applied pressures, between 5–80 bar. In order to reach higher concentration factors, more advanced membrane geometries, such as spiral-wound membranes, could be tested to increase the surface area of the membrane in the RO cell. The RO module used in this experimental system consists of two main components: the pressure pump driving the alkaline feed solution and the RO cell. Prior to the integration of all three subsystems, the initial feed solution will be a 0.6-M potassium hydroxide solution equilibrated with air by bubbling air with a controlled CO<sub>2</sub> partial pressure through a reservoir. The pressure pump can reach up to 80 bar (typical seawater desalination pressures), allowing for an osmotic separation of more than 1 M of NaCl equivalent ions across the RO membrane and reaching a concentration factor of 2. A lower feed concentration of 0.1 M-concentrated by a factor of 10 reaching 1 M—is also being tested and compared to CDI experiments.

#### Concentration Step Using CDI

CDI provides an alternative mechanism for concentrating the alkaline solution. CDI is a method of concentrating and removing anions and cations from solution by applying voltage across two electrodes, adsorbing anions to the positive electrode and cations to the negative electrode to dilute the solution. When the voltage is switched off, the release of the adsorbed ions creates a high-alkalinity brine, which constitutes the concentrating step of the ACS.

CDI systems operate best in brackish water conditions, with salt concentrations below 200 mM, and early-stage CDI systems have been commercialized for desalination, wastewater remediation, and water softening. The effective operation of CDI in this range makes it a candidate for optimal implementation of the ACS at lower salinity. The ability to work at lower initial concentrations enables larger concentration swings that have a larger yield and can thus result in significantly lower energies per unit CO<sub>2</sub> outgassed, as shown in Figure 1. Furthermore, CDI may enable outgassing directly within the concentration module, using gas diffusion electrodes, providing an option for continuous cycling by avoiding the need for a separate outgassing chamber.

Unlike RO systems, commercial CDI systems are less mature and are not designed to be gas-tight, so most commercially available systems are not appropriate for experiments. Because CDI systems do not require high pressure for operation, it is straightforward to create customized test cells at the lab scale and at relatively low cost. The CDI module, at its most basic, consists of a chamber in which the alkaline, air-equilibrated feed solution can come into contact with two electrodes. A type of "sandwich" CDI device is being used, in a "flow-by" configuration, to allow for continuous cycling and reproducible experiments with controllable electrode size, surface area, and cell geometries.

#### System Integration: Full Demonstration of ACS Cycle

After independently testing each of the three components of the ACS approach—(1) concentration of an alkaline solution, (2)  $CO_2$  extraction, and (3) dilution and re-equilibration with air—the combined system can be tested to demonstrate the full ACS cycle. Testing of the full system involves verifying that the carbon removed by the integrated system matches the predicted values for each swing from the theoretical ACS predictions. The energy required for each swing is also measured to determine an overall energy requirement per mole of captured  $CO_2$ . This integration of the three modular components of the experimental system achieves a Technology Readiness Level (TRL) of 3. Based on estimates of the energy requirement for RO in standard saltwater conditions, estimates suggest the ability to achieve  $CO_2$  capture at an energy below 2.0 MWh per tonne of captured  $CO_2$  (265 kilojoule [kJ]/mol). Beyond TRL 3, this requirement could be improved upon by implementing pressure-retarded osmosis, enabling energy recovery when concentrated and diluted solution streams are recombined. Based on estimates of the energy requirement for CDI in standard brackish water conditions, it is estimated to achieve  $CO_2$  capture at an energy of 1.9 MWh per tonne of captured  $CO_2$  (300 kJ/mol). Because electricity flows in the reverse direction when the electrodes are switched off, CDI enables energy recovery; the literature commonly reports energy recovery of 50%, with some studies approaching 80%. However, there is no specific energy target required to achieve TRL 3.

# technology advantages

- Process utilizes well-established, commercially available technologies, including RO and CDI.
- In the RO method, higher feed concentration outgasses more CO<sub>2</sub> for the same concentration factor and higher concentration factor outgasses more CO<sub>2</sub> for the same feed concentration.

# R&D challenges

- Assembling a crossflow RO system.
- Prototyping CDI cells with a larger electrode mass-to-cell volume ratio.
- Building a fully operational CDI model with small volume handling.
- Implementing bicarbonate selectivity with anion exchange membranes.
- Assembling an integrated system and conducting a full demonstration of the ACS cycle.

## status

Harvard University has developed and assembled a dead-end RO system and achieved operating conditions comparable to published systems. Current efforts involve assembling crossflow RO systems and performing kinetic modeling of the experimental results. Researchers have also assembled the CDI system and the initial experimental work indicated operation is comparable to published brackish water CDI systems. Their CDI experiments revealed that higher initial concentrations do not yield larger current or overall capacitance; that higher flow rate, spacer thickness, and cell compression all improve the cell operation; and that a fluid handling system for moving and measuring small volumes is necessary for detecting high concentration factors. Current efforts involve completion of testing the process subsystems and construction of the integrated ACS system.

# available reports/technical papers/presentations

Daniel P. Schrag, Michael J. Aziz, "Experimental Demonstration of Alkalinity Concentration Swing for Direct Air Capture of CO<sub>2</sub>," Direct Air Project kickoff meeting presentation, Pittsburgh, PA, February 2021. https://netl.doe.gov/sites/default/files/netl-file/21DAC\_Schrag.pdf.

Daniel P. Schrag, Michael J. Aziz, Andrew Bergman, Anatoly Rinberg, "Experimental Demonstration of Alkalinity Concentration Swing for Direct Air Capture of CO<sub>2</sub>," kickoff meeting presentation, Pittsburgh, PA, November 2021. http://www.netl.doe.gov/projects/plp-

download.aspx?id=12414&filename=Experimental+Demonstration+of+Alkalinity+Concentration+Swing+for+Direct+Air+Capture+of+CO2.pdf.