

Carbon Dioxide Capture from Atmospheric Air Using Sodium Hydroxide Spray

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In contrast to conventional carbon capture systems for power plants and other large point sources, the system described in this paper captures CO₂ directly from ambient air. This has the advantages that emissions from diffuse sources and past emissions may be captured. The objective of this research is to determine the feasibility of a NaOH spray-based contactor for use in an air capture system by estimating the cost and energy requirements per unit CO₂ captured. A prototype system is constructed and tested to measure CO₂ absorption, energy use, and evaporative water loss and compared with theoretical predictions. A numerical model of drop collision and coalescence is used to estimate operating parameters for a full-scale system, and the cost of operating the system per unit CO₂ captured is estimated. The analysis indicates that CO₂ capture from air for climate change mitigation is technically feasible using off-the-shelf technology. Drop coalescence significantly decreases the CO₂ absorption efficiency; however, fan and pump energy requirements are manageable. Water loss is significant (20 mol H₂O/mol CO₂ at 15 °C and 65% RH) but can be lowered by appropriately designing and operating the system. The cost of CO₂ capture using NaOH spray (excluding solution recovery and CO₂ sequestration, which may be comparable) in the full-scale system is 96 \$/ton-CO₂ in the base case, and ranges from 53 to 127 \$/ton-CO₂ under alternate operating parameters and assumptions regarding capital costs and mass transfer rate. The low end of the cost range is reached by a spray with 50 μm mean drop diameter, which is achievable with commercially available spray nozzles.

Introduction

To mitigate climate change, deep reductions in carbon dioxide (CO₂) emissions will be required in the coming decades. Given the extent of emissions reductions needed to stabilize atmospheric CO₂ concentrations and the inertia involved in shifting the world's primary energy sources from fossil fuels to other alternatives, carbon capture and storage (CCS) will likely constitute a substantial share of emissions reduction in the next half-century.

Nearly all current research on CCS focuses on capturing CO₂ from large, stationary sources such as power plants. Such plans usually entail separating CO₂ from flue gas, compressing it, and transporting it via pipeline to be sequestered underground. In contrast, the system described in this paper captures CO₂ directly from ambient air ("air capture"). This strategy will be expensive compared to capture from point sources, but may nevertheless act as an important complement, since CO₂ emissions from any sector can be captured, including emissions from diffuse sources such as aircraft or automobiles, where on-board carbon capture is very difficult and the cost of alternatives is high. Additionally, in a future economy with low carbon emissions, air capture might be deployed to generate negative net emissions (1). This ability to reduce atmospheric CO₂ concentrations faster than natural cycles allow would be particularly desirable in scenarios where climate sensitivity is on the high end of what is expected, resulting in unacceptable shifts in land usability and stress to ecosystems.

Previous research has shown that air capture is theoretically feasible in terms of thermodynamic energy requirements, land use (2), and local atmospheric transport of CO₂ (3). To assess the practical feasibility of air capture, example systems using current technology have been proposed (1, 2, 4). The proposals generally include a sodium hydroxide (NaOH) or calcium hydroxide (Ca(OH)₂) solution which absorbs CO₂ and is regenerated using the kraft chemical recovery process, an industrial process to recover NaOH (caustic) from Na₂CO₃ used in pulp and paper mills and other industries (5). The CO₂ released during the caustic recovery process can be separated and compressed with methods similar to those for capture from other point sources. A diagram of an example air capture system is presented in Supporting Information (SI) Figure S11.

The component of the system which makes contact with air to extract CO₂ (which we term the "contactor") is the least-proven piece of the system. Suggested forms include large convection towers (6), open, stagnant pools (7), and packed scrubbing towers. As far back as the 1940s, researchers have explored packed tower systems using caustic solution to absorb atmospheric CO₂ for purposes other than climate change mitigation (8–10). Recently, Baciocchi et al. (11) and Zeman (4) considered packed-tower systems with NaOH solution to capture atmospheric CO₂ for climate change mitigation, estimating energy requirements of 30 kJ_e/mol-CO₂ and 88 kJ_e/mol-CO₂ captured, respectively, with varying absorber designs and input parameter assumptions, but neither estimated the cost of capture.

Because CO₂ is so dilute in air, the contactor must have a large cross-sectional area and process large volumes of air with a very low pressure-drop compared with typical industrial gas-absorption processes. For example, a contactor must process roughly 1000 times the volume of air per unit CO₂ of an amine-based system scrubbing power plant flue gas. A packed-tower system may be engineered to these specifications, but the extremely wide and flat form required would be a significant departure from typical systems (11). An alternative strategy is to generate a fine spray of the absorbing solution through an open tower. This strategy has the potential to operate with a small pressure drop in air and avoids the capital cost of packing material, but in trade requires more energy for the pumping solution and creating the spray. A spray-based contactor was proposed in Keith et al. (1) with a very simplistic estimate of cost and energy requirements. Our paper takes a much more sophisticated approach, particularly with the addition of a drop coalescence

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model, to estimate the cost and energy requirements of a spray-based contactor, and corrects an error in the mass transfer calculation of the earlier paper, which had incorrectly assumed air-side limitation to mass transfer.

In addition to energy requirements, a natural concern for any large-scale aqueous contacting system is the quantity of water lost by evaporation. Water loss may be particularly large in an air capture system since the low concentration of CO₂ in the atmosphere requires a large amount of interaction between the gas and liquid phases. Water loss in proposed systems has not been previously calculated or addressed.

The objective of this research is to determine the feasibility of a NaOH spray-based contactor for use in an air capture system by estimating the cost and energy requirements per unit CO₂ captured. We first discuss the theory and modeling methods for CO₂ absorption by a spray, including numerical methods to account for collision and coalescence of drops, and methods to estimate the cost of a full-scale contactor. We then test a prototype contactor to measure CO₂ absorption compared to theoretical predictions, determine the quantity of water lost to evaporation, and calculate the energy requirements of operating the system. Finally, we present the results of an engineering-economic analysis of a full scale contactor and its implications for air capture as a feasible technology to reduce atmospheric CO₂ concentrations.

Materials and Methods

Theoretical Methods. *Mass Transport for a Single Drop.* To determine the feasibility and inform the design of a NaOH spray system, we applied theoretical models to estimate the mass transfer to a drop of NaOH solution falling through air at terminal velocity. In principle, mass transfer may be limited by gas-phase transport, liquid phase transport, liquid phase reaction, or a combination. Comparing a liquid-side limited model given by Danckwerts (12), and a gas-side limited model given by Bird et al. (13, 14), we find that liquid phase transport and reaction is limiting for a falling drop, consistent with previous findings for wetted surface systems (10, 12, 15) (details of the gas-side model and a comparison are given in the SI). The liquid-side limited model is described below. For the dominant sizes of drops used in our prototype (drop diameter, ~100–400 μm), internal circulation does not occur (14), so a simple reaction-diffusion model can be used to estimate the rate of CO₂ absorption. Our system can be approximated by a pseudo-first-order, irreversible reaction at steady state, so the rate of absorption per unit surface area is given by Danckwerts (12):

$$J_{\text{CO}_2} = CK_{\text{H}}\sqrt{D_1 k\{\text{OH}^-\}} \quad (1)$$

where C is the concentration of CO₂ in bulk air, K_{H} is the Henry's constant in the form of the ratio of CO₂ concentration in air to CO₂ concentration in water at equilibrium, D_1 is the diffusion rate of CO₂ in solution, and $\{\text{OH}^-\}$ is the activity of hydroxide ions (primarily a function of NaOH concentration in solution). The reaction constant, k , refers to the reaction (12):



This is a second-order reaction, however the concentration of OH⁻ is so large in our system (> 1 M) that it can be treated as a pseudo-first-order reaction in CO₂. Each of the factors K_{H} , $\{\text{OH}^-\}$, and D_1 is a function of the species present in the solution (especially the ionic strength and viscosity) and temperature. In later calculations, we use the modified Pitzer model (16) to calculate $\{\text{OH}^-\}$ for a given concentration, adjust K_{H} for ionic strength based on data for NaCl solutions (17), and adjust D_1 for solution viscosity effects (18). We assume

$k = 8.5 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (19) and a temperature of 20 °C. See the SI for a detailed discussion of the calculation of k_{spray} (from eq 1) and a table of the parameter values used.

Equation 1 gives the CO₂ absorption rate per unit liquid surface area. We can make a simple estimate of CO₂ absorbed in a contactor by assuming a field of isolated drops of diameter d , falling at terminal velocity. Let ΔM_{pass} be the quantity of CO₂ absorbed on a single pass through the contactor per unit solution volume. We estimate the residence time, τ , of a drop in the contactor by $\tau = H/[v_{\text{air}} + v_t(\text{mdit} > d)]$ where v_{air} is the average vertical velocity of air in the contactor, H is the height of the contactor, and $v_t(d)$ is the terminal velocity of a water drop of diameter d falling in air, as approximated by Wobus et al. (20). The resulting absorption per pass is obtained by multiplying J_{CO_2} (eq 1) by τ , multiplying by drop surface area and dividing by the volume of a drop:

$$\Delta M_{\text{pass}} = \frac{6CK_{\text{H}}H}{d[v_{\text{air}} + v_t(d)]}\sqrt{D_1 k\{\text{OH}^-\}} \quad (3)$$

This is a simplified model applied to the drops in the contactor, but it provides useful insight to the properties of a spray system. In particular, note from eq 3 that CO₂ absorption should increase linearly with H and with the square root of hydroxide activity. Also, for small v_{air} , and if we approximate $v_t \propto d$ (a good assumption for drops in the size range leaving our experimental nozzles) then $\Delta M_{\text{pass}} \propto d^{-2}$.

Mass Transport for a Spray. Small drops tend to collide and coalesce into larger drops, reducing drop surface area and thus the CO₂ absorption rate as they fall. We use numerical methods to model the evolution of drop sizes in a contactor.

We assume that the collision rate is driven by differential settling (larger drops fall faster and collide with smaller drops), but there are competing effects on drop size as some collisions result in coalescence of the drop, while others result in breakup into hundreds of smaller drops. Here we consider only coalescence and spontaneous breakup of drops when they reach an unstable size ($d > 5$ mm), and ignore collisional breakup. The model results will be, in this sense, an upper-bound estimate of the adverse effect of coalescence on CO₂ absorption.

The rate of collisions, R_{12} between a collection of larger drops of diameter d_1 , and smaller drops of diameter d_2 is given by (21–23)

$$R_{12} = N_1 N_2 \frac{\pi}{4} (d_1 + d_2)^2 E_c(d_1, d_2) [v_t(d_1) - v_t(d_2)] \quad (4)$$

where N_1 and N_2 are the number densities of d_1 and d_2 drops, v_t is the drop's terminal velocity, and E_c is the collision efficiency for drops of those sizes passing within geometric alignment (the odds that they will collide as opposed to slip around each other). The collision rate for each drop size is calculated by dividing a continuous distribution of drop sizes into discrete size bins and applying eq 4 for every possible pair of sizes.

To estimate the surface area of spray in a full-scale contactor, we adapted and extended a numerical model developed for cloud aerosol physics (24). The drop size distribution of the spray nozzle is approximated as log-normal and represented by a number and mass of particles in 50 size bins. At each time step, eq 4 is applied using empirical fitted formulas for v_t (20) and E_c (22). The mass and number of drops in each bin is then updated by the method of Tzivion et al. (25) as implemented by Adams and Seinfeld (24). The distribution is then further updated to reflect addition of fresh spray, spontaneous breakup of drops having $d > 5$ mm, and gravitational settling according to the terminal velocity of each drop size.

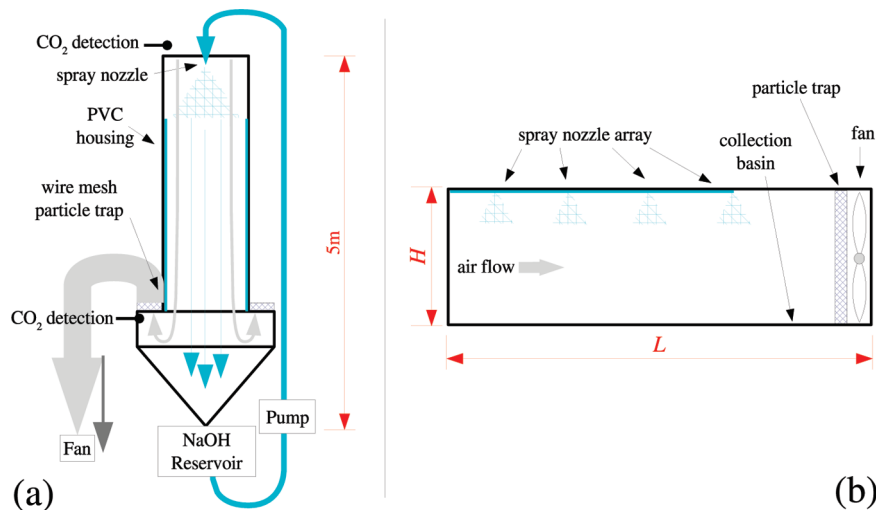


FIGURE 1. (a) Diagram of prototype contactor. Atmospheric CO₂ is absorbed by NaOH spray. CO₂ concentration at the air intake and outlet is measured and the rate of CO₂ absorption is calculated. Working fall height ≈ 3.8 m, geometric wall area ≈ 14 m². (b) A channel in suggested full-scale contactor design. Many such channels would be arranged side-by-side, contained by a hanger-like structure.

Two spatial variants of the model were used to bound the problem, i.e. one case ignores vertical mixing and the second assumes vertical mixing at a 1 m length scale. In the first, the contactor was approximated by a continuous-flow stirred tank reactor (CFSTR) in which drops are assumed uniformly distributed throughout; fresh spray addition and the rate of settling reflect uniform distribution. In the second variant, the height dimension is resolved and the contactor is represented by a stack of layers, each of which is modeled as a CFSTR. Air flow is purely horizontal (Figure 1b) so drops move from one layer to the one beneath by gravitational settling at terminal velocity. Spray is added to the top layer, and drops are removed when they settle from the bottom layer. Reality will be in between these two idealizations: some mixing would occur due to turbulent diffusion, and vertical air flow would be induced by the falling drops. Our base case cost estimate uses the average of the two results.

This model yields spray surface area per unit contactor volume, S . To estimate CO₂ absorption from this, we define the CO₂ absorption rate constant, k_{spray} , such that

$$\frac{dC}{dt} = Sk_{\text{spray}}C(t) \quad (5)$$

Then k_{spray} is the absorption rate per unit CO₂ in air per unit drop surface area, given by J_{CO_2}/C (eq 1).

The rate of CO₂ uptake depends on C , which changes over time. To account for depletion of CO₂ in air as it passes through the contactor, we approximate S as uniform along the length of the contactor and use the concentration, C_{avg} , that yields the average rate of uptake over the contactor (see SI for the derivation of C_{avg}). For a full-scale contactor (Figure 1b), the rate of CO₂ capture of the contactor per unit floor area (denote; \dot{M}) is then (from eq 5)

$$\dot{M} = k_{\text{spray}}C_{\text{avg}}SH \quad (6)$$

whereas in the height-resolved model, S is the average over all cells.

Evaporative Water Loss. For the contactor designs studied here, we will find that the rate of water loss is large enough that the air leaving the contactor would be saturated with water vapor. In this case, we can estimate evaporative water loss by assuming the air leaving the contactor has water partial pressure equal to the vapor pressure of water at the surface of the drops. This calculation provides an upper-bound on evaporative water loss.

For simplicity we assume that air and liquid reach the outlet of the contactor at the same temperature, so that an energy balance yields the temperature at the outlet (assuming contactor materials have reached thermal equilibrium and neglecting the small contribution of the CO₂ enthalpy of dissolution):

$$T_{\text{out}} = T_{\text{in}} - \frac{\Delta C_{\text{H}_2\text{O}}\Delta H_{\text{vap}}}{\rho_{\text{air}}C_{p,\text{air}} + \rho_l c_l} \quad (7)$$

where $C_{p,\text{air}}$ and c_l are the heat capacities of air and the liquid solution (assumed equivalent to water), and ρ_{air} and ρ_l are the bulk densities of air and suspended solution. The quantity of water evaporated, $\Delta C_{\text{H}_2\text{O}}$, is the difference between the inlet water concentration and the water concentration corresponding to the vapor pressure of the solution:

$$\Delta C_{\text{H}_2\text{O}} = C_{s,\text{H}_2\text{O}}(T = T_{\text{out}}) - C_{\text{H}_2\text{O},\text{in}} \quad (8)$$

Equations 7 and 8 are solved simultaneously by iteration to yield $\Delta C_{\text{H}_2\text{O}}$. Knowing the overall capture efficiency for the contactor of CO₂ from air allows a calculation of water loss per unit CO₂ absorbed.

Experimental Methods. We constructed a prototype contactor to measure CO₂ capture by NaOH spray and to measure the energy requirements in a way that is relevant to full-size contactors.

Figure 1a shows a schematic drawing of the apparatus (see photographs in the SI, Figures SI3–SI4). NaOH solution is sprayed through the tower, collected, and recirculated from a 15 L reservoir while air is blown down through the tower concurrently at approximately 0.4 m/s. Though it sacrificed some efficiency over an upward-flow design, the downward-flow, cocurrent design allowed for simpler construction and maintenance of the particle trap system. CO₂ concentration in inlet and outlet air was measured using a LiCOR (Lincoln, NE) infrared gas analyzer. Carbonate (CO₂) concentration was measured in periodic liquid samples using a Shimadzu (Kyoto, Japan) total carbon analyzer to corroborate the LiCOR measurements. Additionally, temperature, relative humidity, and pressure drops were recorded. More detailed explanation of the experimental apparatus is given by Stolaroff (26).

Two single-fluid spray nozzles producing uniform, full-cone spray patterns were used: a spiral-tip nozzle from Allspray (Carol Stream, IL) with a higher flow rate and larger drop size (the “high-flow nozzle”), and a swirl-chamber

nozzle from Delavan (Bamberg, SC) with a lower flow rate and smaller drop size (the “low-flow nozzle”). Drop size data from the manufacturer were available for the high-flow nozzle and were used to compare experimental data with theoretical CO₂ absorption. Experiments were run with nozzle pressures ranging from 100 to 620 kPa.

We tested three NaOH concentrations. A 0.35 M solution represented a dilute state, with viscosity and vapor pressure about the same as water. A 5 M solution, about 20 wt% NaOH, represented a high-concentration solution which has a viscosity about 3 times that of water and is hygroscopic in some climatic conditions. 1.33 M served as an intermediate concentration (each concentration differs by about a factor of 4).

Cost Estimation. To estimate the cost of CO₂ capture by a contactor used in a future full-scale air capture system, we considered a cross-flow design with the air traveling through a horizontal channel (Figure 1b). Structurally, the contactor has a minimal steel frame with corrugated metal or fiberglass skin, analogous to an aircraft hanger or very tall warehouse. The walls and roof serve only to support the spray system and to minimize air exchange and fugitive particle emissions. The floor is a concrete slab with a drainage system to collect spray. Support columns are spaced to minimize construction cost. The structure or set of structures will be large enough in area that capital cost is essentially constant per unit floor area. Component costs such as pumps, nozzles, and the particle trap are not included explicitly; however, as a check on the capital cost estimates discussed below, a rough cost of each of these is calculated in the SI, and even with conservative assumptions comprise not more than 10% of the total capture cost per ton CO₂ in our base case.

We consider three main components of the contactor cost: capital, operation and maintenance, and electricity for operating pumps and fans. Though there are other costs, we expect these to dominate. Each is calculated per unit of CO₂ captured.

Energy Requirements. Electricity is used by pumps to lift solution up the height of the tower and to overcome the pressure drop across the nozzle, ΔP_{nozzle} . Fans use electricity to overcome the pressure drop in air across the contactor, which is dominated by the particle trap, and to accelerate the air. Frictional losses are considered comparatively small and are neglected.

The theoretical lifting energy per unit solution is simply $\rho_{\text{soln}} \cdot g \cdot H$, where ρ_{soln} is the density of solution and g is the acceleration due to gravity. Recall that in the single drop model, CO₂ absorption is also linear with H so that lifting energy per unit CO₂ will be approximately constant. When accounting for coalescence, lifting energy per unit CO₂ increases with H because the spray becomes less efficient as H increases. In contrast, pumping energy to overcome ΔP_{nozzle} is constant with H , and so nozzle energy per unit CO₂ decreases with H , inverse-proportionally in the single-drop case, and less quickly with coalescence. Fan energy is essentially fixed per unit of air passing through the contactor, and so fan energy per unit CO₂ is inversely proportional to ΔC .

From an energy-efficiency perspective, the design of the contactor is constrained to have a spray residence time (i.e., H) long enough to scale down the nozzle pressure energy and, because of coalescence, to be short enough that lifting energy does not become overwhelming. These constraints drive our choice of H . The cross-flow design allows us to introduce another parameter, L , the length of the channel in the direction of air flow, which can be selected for optimum ΔC to minimize fan energy, independent of H .

In our cost calculations, the rate of energy use by pumps is given by

$$\dot{E}_{\text{pump}} = \frac{F}{\epsilon_{\text{pump}}} (\Delta P_{\text{nozzle}} + \rho_{\text{soln}} g H) \quad (9)$$

where F is the liquid flowrate and ϵ_{pump} is the mechanical efficiency of the pump. We assume $\Delta P_{\text{nozzle}} = 350$ kPa (a reasonable value based on our experiments and our survey of commercial nozzles, though smaller pressure-drops may be possible) and $\epsilon_{\text{pump}} = 0.85$.

For fan energy, it is more convenient to use energy per unit CO₂ captured, \dot{E}_{fan}/M , than absolute energy:

$$\frac{\dot{E}_{\text{fan}}}{M} = \frac{\Delta P_{\text{air}} + \frac{1}{2} \rho_{\text{air}} v_{\text{air}}^2}{\epsilon_{\text{fan}} \Delta C} \quad (10)$$

where ρ_{air} is the density of air and ϵ_{fan} is the fan efficiency, taken as 0.85.

Capital Cost and Maintenance. To estimate the cost of building a full-scale contactor, we consulted several construction industry experts working at different firms in the United States and Canada. We gave them the structural description above and explained the application in detail. They returned estimates of installed cost per unit floor area of 1000 \$/m², 250–750 \$/m², and 200 \$/m² for a 20 m high structure (this excludes the purchase of land). This is in line with known costs of analogous structures. Some recently constructed aircraft hangers in the U.S. range in cost from 370 to 670 \$/m² (27). Warehouses on average are 700–940 \$/m², which includes plumbing and climate control. We use 500 \$/m² as our best-guess estimate and consider the range of 250–750. All of these are in approximately year 2000 costs, which we believe better reflect the long-run real cost of construction than current, inflated prices. Since air capture is only useful at very large scale, any future system should take full advantage of economies of scale in design, construction, and operation, which may reduce the costs from these estimates.

In addition to these initial construction costs, following the convention for power plant cooling towers (28), we assume the physical operating and maintenance cost of a contactor is 4% of capital per year.

Total Cost. To estimate the total CO₂ capture cost for the contactor, T_c , we assume that carbon-neutral electricity is purchased at the price, p_{elec} , of \$0.07/kW-hr (\$19/GJ). This reflects roughly the cost of base-load electricity from nuclear or CCS plants. We further assume a constant capital charge rate, r , which includes 4%/yr for maintenance and capital investment amortized at 15%/yr in the base case, typical for an electric power industry project, giving $r = 19\%$. However, air capture is arguably likely to be a public endeavor (29), suggesting that a social discount rate would be more appropriate. For this case we amortize capital at 6.5% ($r = 10.5\%$).

Applying the previously presented formulas, and denoting the capital cost by K , we can express the total capture cost by

$$T_c = \frac{K \cdot r + p_{\text{elec}} (\dot{E}_{\text{pump}} + \dot{E}_{\text{fan}})}{M} \quad (11)$$

where M is given by Equation 6, \dot{E}_{pump} is given by eq 9, and the term \dot{E}_{fan}/M given by equation 10.

Results and Discussion

Mass Transfer. The prototype reactor was used to measure CO₂ uptake by NaOH spray. Outlet CO₂ concentrations during a typical trial of the prototype contactor are shown in Figure 2. CO₂ is absorbed by NaOH spray and by NaOH solution on the walls, reducing the outlet CO₂ concentration compared with the background (inlet). By running the system to steady

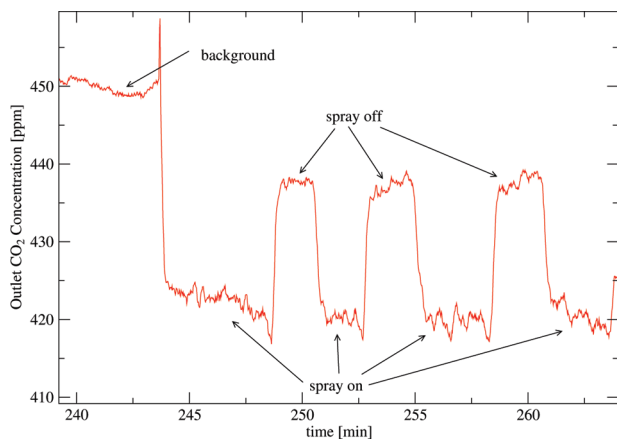


FIGURE 2. Outlet CO₂ concentration during a typical trial. Conditions: [NaOH] = 1.3 M, liquid flowrate = 4 L/min, nozzle pressure = 380 kPa, air/liquid mass flow ratio = 8.3, estimated suspended spray surface area = 8 m², working fall height ≈ 3.8 m, estimated spray residence time τ = 3 s, geometric wall area ≈ 14 m².

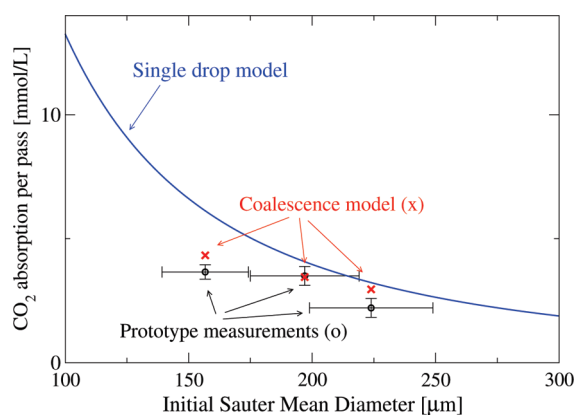


FIGURE 3. Comparison of CO₂ absorption predicted by single-drop model and by coalescence model with prototype measurements. Circles represent measured aggregate absorption by a spray with the indicated initial Sauter mean diameter, as inferred from nozzle manufacturer reported data for flow rate and drop size as a function of nozzle pressure and fitted size distribution (all points with high-flow nozzle and 1.3 M solution). Error bars represent combined subjective uncertainties and standard error of repeated measurements. X's indicate coalescence model result for the same conditions of the experimental point nearby.

state then suddenly turning the spray off we can isolate absorption by the spray from absorption by the wetted walls. Figure 2 shows several on-off cycles. The absorption rate is calculated from the average difference in peak heights. Under the conditions in this trial, 17 ppm of CO₂ is absorbed by the spray and 17 ppm by the wetted wall from the air passing through the system. Considering just the spray effect, that is a CO₂ absorption rate of 3.7 mmol per liter of solution per pass, roughly equivalent to 0.4 ton-CO₂/yr per m² of contactor cross-section.

By adjusting nozzle pressure with other parameters held constant, we measured the effect of drop size on CO₂ absorption for 1.3 M solution. The effect of NaOH concentration on absorption was also measured (see SI Figure SI5). Measured CO₂ uptake and manufacturer-reported data on the flow rate and volume-median drop diameter at each pressure (30) was used to estimate CO₂ absorption per liter of solution as a function of drop size. The results are shown as the circles in Figure 3. This plot also shows the comparable single-drop model results and coalescence model output for the conditions of each trial using the theoretical k_{spray}

(accounting for ionic strength and viscosity effects, see SI). In both cases, the nozzle spray distribution was assumed to be log-normal with the volume-median drop size reported by the manufacturer and geometric standard deviation $\sigma = 1.6$, which corresponds to the average distribution width for a full-cone pressure-swirl nozzle reported by Spielbauer (31). On average, CO₂ absorption agreed with theory within 20%. This agreement with theory indicates that the use of theoretical values is justified. We use the theoretical k_{spray} for 2.5 M NaOH in our base-case cost calculations.

Water Loss. Evaporative water loss was measured in two trials. For example, with a 1.3 M solution with negligible carbonate loading, $T = 19$ °C, and inlet relative humidity (RH) of 50%, it was 80 mol-H₂O per mol-CO₂ (30 m³/ton-CO₂). As expected, this is high enough that air leaving a full-scale contactor is likely to be saturated in water. Thus, to estimate full-scale water loss we can apply eqs 7 and 8. A contactor capturing 30% of CO₂ from air would lose about 30 mol-H₂O per mol-CO₂ under these conditions, which were warm and dry in global climatic terms. A more typical temperature of 15 °C and RH of 65% gives water loss of 20 mol/mol for a 1.3 M solution.

Water loss could impose an important constraint on the deployment of these systems. If we consider a system with evaporative water loss of 20 mol-H₂O/mol-CO₂, and capture all U.S. transportation sector CO₂ emissions, we would need 2×10^{10} m³/yr of water (32). This is roughly equal to half-the evaporative loss from all thermoelectric power cooling and to half-the total nonpower industrial water use in the U.S (33).

Higher-molarity NaOH solutions, having lower vapor pressure, lose less water to evaporation. At 15 °C and 65% RH, a NaOH concentration of 7.2 M is sufficient to eliminate all water loss. However, as the solution absorbs CO₂ and carbonate loading increases, vapor pressure and water loss may also increase relative to pure NaOH. The desirable level of carbonate loading will depend on the caustic recovery system (the carbon absorbed by the solution in a single pass through the contactor is small; higher loadings can be achieved by recirculation). We expect that in a full-scale system water loss can be managed by adjustment of the NaOH concentration in temperate or humid climates. Even with lower-molarity solutions, the cost of makeup water is not prohibitive assuming a typical industrial water price of \$0.13/m³ (34); however, sources of water and the required water quality must be considered.

Prototype Energy Requirements. Energy per unit CO₂ in the prototype was calculated from the height of the contactor and the pressure reading near the nozzle, along with the measured CO₂ absorption rate. For lifting energy, values obtained covered the range 6.0–24 kJ/mol-CO₂. The best (lowest) value was for the 5 M solution and low-flow nozzle. The nozzle energy for this trial was 90 kJ/mol at the high nozzle pressure of 590 kPa. The lifting energy in a full-scale system would be larger due to coalescence, but the nozzle energy would be much lower due to a higher spray residence time (τ), and likely lower nozzle pressure.

The fan energy is calculated from the pressure difference measured between the inlet (ambient pressure) and the duct following the mesh particle trap, ΔP_{air} Pa. This gives 290 kJ/mol for the same trial discussed above. However, in a larger system, this would scale inversely with ΔC . Additionally, commercially available particle traps can operate at a lower pressure drop. Based on discussions with manufacturers, we use $\Delta p = 40$ in the cost estimate. For both of these reasons, fan energy will likely be a small fraction of this a full-scale system.

Total energy requirements for the prototype ranged from 190 to 390 kJ/mol for various conditions. However, this is

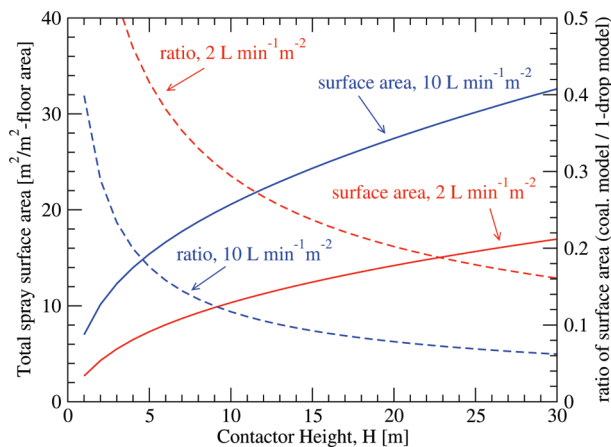


FIGURE 4. Drop surface area in a cross-flow contactor as a function of contactor height as predicted by the coalescence model. Shown on the left axis as the total surface area per unit contactor floor area (solid line), and on the right axis as a ratio against the no-coalescence single-drop model (dashed line).

not likely to reflect total energy requirements in a full-scale system for the reasons discussed above.

Total Cost. Since full-scale systems will have longer drop residence times and denser sprays than the prototype, we expect coalescence to be important. Indeed, it turns out to drive contactor design. Figure 4 shows the total drop surface area predicted by the coalescence model as a function of height. The solid line, depicting total surface area per unit contactor floor area, shows quickly diminishing returns to additional fall height. Since CO_2 absorption is proportional to surface area, this indicates little additional absorption for the added capital expense of higher structures. Looked at another way, the ratio of surface area with coalescence to what would be expected by the no-coalescence, single-drop model (dashed lines) is a measure of the efficiency of the spray. The required lifting energy is inversely proportional to this efficiency, so tall contactors become expensive in pumping energy as well as capital.

Considering these features and the practicality and cost of different structures, we select $H = 20$ m for our cost calculation. The length of the air channel, L , is chosen to achieve a target ΔC . The capital cost of the demister and the fan energy (both inversely proportional to ΔC) turn out to be small in the cross-flow design, so we use a relatively small 30% capture efficiency from air to keep C_{avg} high. For a fixed ΔC , L is proportional to the air speed, v_{air} , which does not otherwise have a substantial role in the cost calculation, so we choose a small but practical $v_{\text{air}} = 2$ m/s. These choices give the fan energy, $\dot{E}_{\text{fan}}/\dot{M}$ of 8.4 kJ/mol.

We now have all but one parameter needed to calculate the capture cost. Both \dot{E}_{pump} and \dot{M} depend on the liquid flow rate, F . A higher f provides more drop surface area (Figure 4), allowing more CO_2 to be captured per unit floor area, reducing the cost of capital per unit CO_2 . However, higher spray densities lead to more coalescence and reduced absorption efficiency, thus increasing the energy requirement per unit CO_2 . Figure 5 (solid curves) shows the total cost per unit CO_2 captured (Equation 11) over a range of F . The lowest-cost optimum is at the bottom of the curve, at 96 \$/ton- CO_2 and $F = 10$ $\text{L min}^{-1} \text{m}^{-2}$, though energy requirements (dashed curve) are large at this point, about 94 kJ/mol. Because the cost curve is relatively flat here, the energy requirement can be reduced to 76 kJ/mol at essentially the same total cost with $F = 7$ $\text{L min}^{-1} \text{m}^{-2}$, or to 53 kJ/mol for a 10% increase in total cost. Accordingly, different assumptions about the energy price will tend to shift the cost-optimum.

The energy requirement may be compared with the heat of combustion of, for instance, gasoline, which is roughly

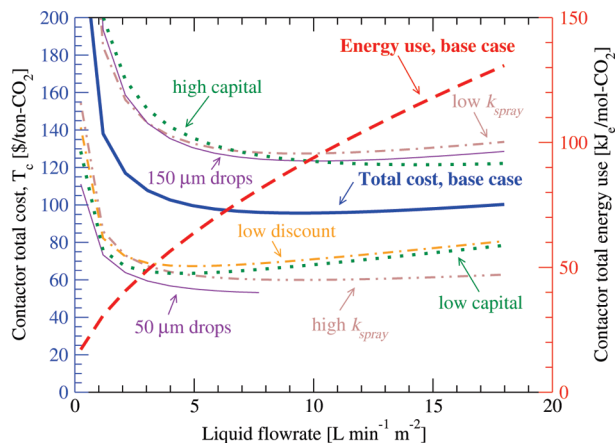


FIGURE 5. Base-case contactor total cost (left axis, thick solid line) and energy use (right axis, thick dashed line) as a function of liquid flow rate. The base case assumes the nozzle mean drop diameter is 100 μm , capital cost is \$500/ m^2 amortized at 19%/yr, and $k_{\text{spray}} = 2.5 \times 10^{-3}$ m/s (i.e., 2.5 M NaOH). Thinner or dashed lines represent total cost assuming larger or smaller mean drop size at the nozzle, higher or lower k_{spray} , higher or lower capital cost, or a social discount rate.

660 kJ/mol- CO_2 (noting that this is thermal energy compared with the electrical energy requirement for pumps and fans). The comparable energy requirement for the pumps and fans in a typical amine-based CO_2 scrubber at a power plant (excluding solvent regeneration and CO_2 compression) is about 5 kJ/mol (35). Thus at about 1 order of magnitude higher energy requirements, we are capturing CO_2 from a gas stream more dilute by 3 orders of magnitude. The energy requirement falls above the estimate from Baciocchi et al. (30 kJ/mol) and is similar to the estimate from Zeman (88 kJ/mol) for air capture with a packed tower. However, unlike these two, the present estimate attempts to make a real tradeoff between energy efficiency and capital cost. In this system, capital cost turns out to be important, resulting in higher energy requirements. It should also be noted that Baciocchi et al. assume an atmosphere with 500 ppm CO_2 , as opposed to our assumption of 400 ppm and Zeman's of 380 ppm (our capture cost and energy requirements are nearly inversely proportional to CO_2 concentration).

The 96 \$/ton capture cost (which excludes the potentially comparable cost of solution regeneration, CO_2 compression, and injection) represents the base-case assumptions. There are several operating parameters that could reduce or increase this cost significantly, including k_{spray} and the spray mean drop size. k_{spray} depends on the composition of the solution, including the concentration of NaOH, carbonate loading, and any additives, however above about 1.5 M NaOH, k_{spray} is relatively insensitive to these values because the increase in rate due to higher $\{\text{OH}^-\}$ is offset by the lower diffusivity of CO_2 in the higher viscosity solution and lower Henry's constant (see SI). A range of k_{spray} of -25 to $+60\%$ (0.0018–0.0040 m/s) includes, on the low end, the value implied by our prototype measurements for 1.3 M solution and, on the high end, the highest k_{spray} calculated from values in the literature for a 2.5 M solution (36). With all else constant, this range gives a range in cost of 60–127 \$/ton (Figure 5).

The base case calculations assume a volume-median drop diameter at the nozzle of 100 μm . However, a survey of commercially available nozzles indicates that much smaller drops are achievable at the same nozzle pressure with water. With all else equal, a median drop size of 50 μm yields of total cost of 53 \$/ton, and this does not account for parameter optimization in accord with the smaller drops, which would reduce costs further. On the other hand, if even 100 μm drops are not practical, we can at least expect to achieve drops in

the size range tested in the prototype, e.g. 150 μm , which gives a cost of 124 \$/ton.

There are several remaining factors important to total cost. The range of capital cost estimates we received (250–750 \$/m²) yields a range in T_c of 64–122 \$/ton with other parameters held constant. A social discount rate (giving a capital charge rate of 6.5% yr⁻¹), as opposed to the industrial rate (i.e., 15% yr⁻¹ capital charge rate) used, would bring the cost down to 67 \$/ton with other parameters constant. Inclusion of collisional breakup in the coalescence model would also provide some cost reduction.

Implications. The prototype demonstrates four key features of a potential NaOH spray-based contactor: (1) off-the-shelf single-fluid spray nozzles can produce a spray which efficiently absorbs CO₂ from ambient air in terms of energy required for lifting the solution, (2) such nozzles can produce such a spray at pressures which are not prohibitive, (3) the pressure drop across a particle trap which controls entrainment of small drops from such a spray is not prohibitive in terms of energy required for blowing air, and (4) from our laboratory experience, materials compatibility, and safety concerns in handling NaOH do not pose significant challenges to the design and operation of a contactor.

Our numerical modeling and range of cost estimates suggest that a full-scale contactor could likely be operated as part of an air capture system for a cost on the order of 100 \$/ton-CO₂, perhaps significantly less with application of appropriate fine-mist spray nozzles. Technology in this cost range may very well be useful to mitigate climate change in a future of high climate sensitivity, rapidly rising sea-levels, or extended inaction on conventional mitigation requiring abrupt emissions reductions.

However, scaling up the mass transfer process observed in the prototype to meet the needs of a global carbon mitigation scheme is a complex engineering challenge. With the base-case contactor running at the cost-optimal flowrate, a structural area of about 760 by 760 m would be required to capture 1 Mt/yr of CO₂. Cost estimates for a full scale contactor were high compared to similar estimates for capture from point sources and the uncertainty range will remain large without a detailed engineering design and additional pilot data. Smaller drop sizes, methods to minimize drop coalescence, solution adjustments to increase k_{spray} , and optimization of contactor design are paths toward improving efficiency. Nevertheless, the straightforward contacting technology presented here appears to be viable at costs relevant to climate policy, and supports the notion that air capture is an option available to society to mitigate climate change that should be seriously considered.

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Nomenclature

C = concentration of CO₂ in bulk air [mol/m³]
 C_{avg} = average concentration of CO₂ inside the contactor [mol/m³]
 $C_{\text{H}_2\text{O},\text{in}}$ = concentration of water vapor in air entering the contactor [mol/m³]
 $C_{\text{s},\text{H}_2\text{O}}$ = concentration of water vapor in air at saturation [mol/m³]
 ΔC = change in CO₂ concentration in air across the contactor [mol/m³]

$\Delta C_{\text{H}_2\text{O}}$ = change in concentration of water vapor in air [mol/m³]

c_l = heat capacity of solution [kJkg⁻¹ °C⁻¹]

$c_{p,\text{air}}$ = heat capacity of air [kJkg⁻¹ °C⁻¹]

D_l = diffusion rate of CO₂ in solution [m²/s]

d = drop diameter [m]

\dot{E}_{pump} = rate of energy use by pumps per unit contactor floor area [kW/m²]

\dot{E}_{fan} = rate of energy use by fans per unit contactor floor area [kW/m²]

F = solution flow rate per unit contactor floor area [m/s] or L min⁻¹ m⁻²

g = acceleration due to gravity [m/s²]

H = contactor height [m]

ΔH_{vap} = heat of vaporization of water [kJ/mol]

J_{CO_2} = CO₂ absorption rate per unit surface area [mol s⁻¹ m⁻²]

k = reaction rate constant of CO₂ with OH⁻ [m³ mol⁻¹ s⁻¹]

k_{spray} = CO₂ absorption rate constant [m/s]

K = contactor capital cost per unit floor area [U.S. \$/m²]

H_{H} = Henry's constant []

L = contactor length [m]

\dot{M} = capture rate of CO₂ per unit contactor floor area [mol s⁻¹ s⁻²] or [ton s⁻¹ s⁻²]

ΔM_{pass} = quantity of CO₂ absorbed per unit solution on a single pass through the contactor [mmol/L]

{OH⁻} = activity of hydroxide ions in solution [mol/m³]

p_{elec} = price of electricity [U.S. \$/kJ]

ΔP_{fan} = pressure drop in air across the contactor [Pa]

ΔP_{nozzle} = pressure drop at the spray nozzle [Pa] or [kPa]

r = capital charge rate [s⁻¹]

S = surface area of spray per unit contactor volume [m²/m³]

T_c = total cost of capture [U.S. \$/ton-CO₂]

T_{in} = temperature of air and liquid entering the contactor [°C]

T_{out} = temperature of air and liquid leaving the contactor [°C]

v_{air} = velocity of air in the contactor [m/s]

$v_t(d)$ = terminal velocity of falling drop with diameter d [m/s]

ϵ_{fan} = mechanical efficiency of fans []

ϵ_{pump} = mechanical efficiency of pumps []

ρ_{air} = density of air [kg/m³]

ρ_l = bulk density of suspended solution in the contactor [kg/m³]

ρ_{soln} = density of solution [kg/m³]

Note Added after ASAP Publication

A department name was missing from the author affiliations and minor typographical errors were present in the version published ASAP March 6, 2008; the corrected version was published March 18, 2008.

Supporting Information Available

More detail on mass transfer calculations, an example air capture system, derivation of the formula for CO₂ depletion in air, photographs of the prototype, and additional experimental results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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