Title: EXTRACTION OF CARBON DIOXIDE FROM THE ATMOSPHERE THROUGH ENGINEERED CHEMICAL SINKAGE

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Abstract

We present the case for CO₂ extraction from air as a means of sustaining fossil energy use by avoiding climate change. Our concept harnesses atmospheric circulation to transport CO₂ to sites where the CO₂ is extracted by binding it to an adsorbent. As a proof of concept, we show that an aqueous Ca(OH)₂ solution efficiently converts CO₂ to a CaCO₃ solid that can be heated to obtain pure CO₂ and recover the CaO. Even with recycling costs, CO₂ extraction from air blown by wind through a 1 m² aperture could eliminate the greenhouse gas impact of 100 kW gasoline engine, making it more favorable than renewable sources as solar, wind, or bio-mass. In addition it collects CO₂ from dispersed sources, preserves the energy infrastructure, can yield negative emissions, and provide free CO₂ transport to sequestration sites. We report economic and scaling arguments, atmospheric simulations and experiments that support pursuing air-extraction as an advanced CO₂ capture technology. This method could process today’s world output of CO₂ with many collection units with a net area of 10³-10⁴ km² at costs of ~$5/liter of gasoline, a manageable scale for this massive undertaking.
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Introduction

The 2001 Third Annual Report of the Intergovernmental Panel on Climate Change projects that atmospheric carbon dioxide (CO₂) can approach 1000 ppm in 2100.¹ In addition it concludes that the observed warming over the last 50 years is likely to have been due to the increase in greenhouse gas concentrations, particularly the 30% rise in atmospheric CO₂ caused by man. Fossil fuel use will be limited by our ability to mitigate their environmental effects since they are abundant and cost effective. Future concerns are underscored by the long lifetime of CO₂ in the atmosphere, the accelerating rate of fossil-fuel consumption, and our non-linear climate system that can migrate to a different state in response to radiative forcing on decadal time-scales. Consequently technologies for reduction of the world’s CO₂ emissions are being explored aggressively. Current emphasis is on fixing CO₂ at large sources such as centralized power plants by emission free conversion of fossil fuels to electricity and hydrogen.² However, more than half of the total emissions is from the transportation sector and small distributed sources such as home heating and small industry. Most solutions for dealing with these sources explicitly or implicitly imply a complete overhaul of the existing infrastructure. To surmount this problem Los Alamos National Laboratory has conceived a novel concept of extracting CO₂ directly from the atmosphere by engineering a chemical sink³,⁴

Direct CO₂ extraction converts the dilute CO₂ (370 ppm) in the atmosphere (from all sources) to a pure CO₂ stream ideal for permanent sequestration. For dealing with the world’s total fossil fuel related CO₂ emission rate, extracting CO₂ from the air involves processing of on the order of up to 1% of the earth’s atmosphere (containing ~750 Gt CO₂) each year. The fast time scales of atmospheric mixing make this approach feasible. It is a massive undertaking with offsetting advantages:

- Preserves our existing energy use and fuel distribution network that represents a huge investment,
- Captures CO₂ from a myriad of small, distributed, and mobile sources that otherwise are not accessible to sequestration,
- Allows atmospheric CO₂ levels to be restored to their pre-industrial age value,
- Provides free transport of CO₂ to suitable sequestration sites by using the natural atmospheric circulation, and
- Is relatively compact and therefore inexpensive approach when compared to renewable concepts.

This method compensates for all CO₂ sources, can be scaled to yield a net zero or negative emissions, and harnesses the atmosphere as a free CO₂ transportation network.

Our CO₂ extraction from air concept is summarized here and developed in more detail later. By equating an amount of CO₂ with the energy released in a combustion process, one can associate an energy density with CO₂ in air. By this measure, the energy associated with atmospheric CO₂ is a factor of approximately 100 times more concentrated than wind energy, which is harnessed routinely. Building on this premise our concept harnesses atmospheric circulation to extract CO₂ from air (where it is present at 370 ppm) and binds it to an adsorbent. The saturated absorbent is subsequently heated to release the bound CO₂ thereby generating a pure CO₂ stream for disposal and adsorbent ready for reuse. Low cost chemical extraction reagents such as calcium hydroxide (a prime ingredient in mortar) readily extract CO₂ and demonstrate the feasibility. The reagents would be continuously recycled with the captured CO₂ being recovered and sent to a permanent disposal process such as the mineral carbonation of serpentinite deposits that permanently sequester the CO₂ as solid, harmless, and inert mineral carbonates,⁵ or direct injection in underground reservoirs or in the deep ocean.

Case for CO₂ Extraction from Air

Concept. To determine the viability of CO₂ extraction from air we compare it to renewable energy options, examining the relative size and therefore likely cost and environmental impact. We also examine the energy requirements of one specific approach to CO₂ capture, which although far from ideal demonstrates feasibility. Our estimates are meant to establish orders of magnitude rather than precise values. The yardstick we employ is the primary energy per unit area and unit time available. We start by examining wind power, which is routinely harvested, albeit on a modest scale. The power per unit area is given by 1/2 ρ v³, where ρ is the density of air and v is its wind velocity. At 10 m/s the wind power contained in the airflow is 0.6 kW/m². The time averaged power flux from sunlight on the ground is less, amounting to 0.2 kW/m² in the US. The equivalent power collected by biomass represents no more than 0.003 kW/m² of heat of combustion amounting to 50% of dry mass hectare⁻¹ year⁻¹.

For the extraction of CO₂ from the atmosphere, we consider the same airflow as for wind power. The 1 m² of air that flows through the 1 m² aperture in one second contain 0.15 moles of CO₂. There is less, amounting to 0.2 kW/m² in the US. The equivalent power collected by biomass represents no more than 0.003 kW/m² of heat of combustion amounting to 50% of dry mass hectare⁻¹ year⁻¹.

For the extraction of CO₂ from the atmosphere, we consider the same airflow as for wind power. The 1 m² of air that flows through the 1 m² aperture in one second contain 0.15 moles of CO₂. There is amount of carbon based fuel without increasing the net CO₂ content of the air. For gasoline we would generate 100 kW/m² of primary energy without any impact on the atmospheric level of CO₂. In contrast, a windmill of the same area would only draw on 0.6 kW/m² of raw power, a factor of over 100 less. Comparison with other renewable resources is even more dramatic.

Process Description. The low CO₂ concentration in air limits the choice of collection methods. Chemical or physical absorption from an essentially free flow atmospheric air stream appears to be the only viable option. For absorption, the primary energy demand lies in the chemical reactions. The free energy of mixing sets a lower bound on the desired output pressure, R, the gas constant, and T, the absolute temperature. Separating CO₂ from air at ambient conditions and delivering the output at 1 bar requires 20 kJ/mole. This is only 3% of the energy released in the combustion of gasoline. However, practical implementations will require more energy for rapid CO₂ absorption and concentration.
As air moves over an absorber surface, CO₂ is stripped out. The rate of extraction depends on the efficiency of the absorber, but even the best absorber is limited by the transport of CO₂ through air. The molecular diffusion coefficient of CO₂ in air at ambient temperature is $D = 1.39 \times 10^{-5}$ m²/s. The mass flux to an absorbing surface is given by $N = D \nabla p_{CO₂} \rho_{CO₂}$, being the local density of CO₂ in the air. For a good absorber, the partial pressure of CO₂ at the absorption surface nearly vanishes, and the mass flux, $N_{0}$, to a boundary is given approximately by $N_{0} = D \rho_{CO₂} / L$. Here, $L$ is the transport distance; i.e., the typical distance to the nearest surface or for an open system the thickness of a boundary layer. As a specific example, consider air flowing at 10 m/s through a set of parallel tubes, 2.5 mm in diameter. Empirical formulae suggest an effective $L = R/1.8$, where $R$ is the radius of the tube. Comparing the CO₂ flux to the wall with the CO₂ flux through the tubes suggests that most of the CO₂ will be removed after ~30 cm. The distance over which the CO₂ is absorbed is proportional to the flow velocity. With a typical velocity of 3 m/s the length of the tube is reduced to less than 10 cm.

In passing over an absorber that removes a portion of the CO₂ from the air-stream, a similar fraction of the air's momentum will be removed, as these two molecular diffusion processes operate similarly. Thus, for a system designed to extract most of the CO₂, the pressure drop is roughly the kinetic energy density in the gas or about 0.06 kPa at 10 m/s. Thus, maintaining the airflow requires an energy input of 0.06 kJ/m², which is less than 1% of the energy released in producing that CO₂. Quite likely, a practical implementation would utilize natural convection or wind for this task.

**CO₂ Adsorption Collection.** Can CO₂ be collected? The common reagent Ca(OH)₂ provides a proof of principle. An aqueous solution of Ca(OH)₂ is very efficient in collecting CO₂ from air. Simply bubbling air through a few centimeters of Ca(OH)₂ solution removes the bulk of the CO₂. The overall resistance to mass transfer is not substantially larger than the transfer resistance in the gas phase. The high degree of extraction that is achieved with Ca(OH)₂ is obtained at the price of a substantial binding energy. The reaction can be summarized as follows: Ca(OH)₂ + CO₂ → CaCO₃ + H₂O + 114 kJ of energy release. The return calcination reaction CaCO₃ → CaO + CO₂ requires 179 kJ/mole, which is the energy penalty for recovering CO₂. While this is a non-negligible fraction of the energy from burning gasoline (~650 kJ/mole CO₂), it is still a manageable amount.

**System Design.** Based on these observations, an idealized process plant would have a number of units, presumably wind or convection driven, that form CaCO₃ from an aqueous Ca(OH)₂ solution. The CaCO₃ precipitate is dried and calcined, which requires energy. The energy for drying could be provided by the heat of hydration when CaO is transformed back into Ca(OH)₂. However, calcination would require additional energy, which can come from a number of sources. To be specific, we assume that it is provided by the combustion of coal. The amount of CO₂ generated in the combustion is about 40% of what is stored on the sorbent. Since the process operates on a large scale and is obviously located at a disposal site, the CO₂ from the coal would be directly captured and disposed of.

**Cost and Economics.** To estimate costs we assume that the cost per unit area of airflow is the same for a windmill and a CO₂ absorption unit. This assumption is justified, since lightweight structures covered with a film of calcium hydroxide solution would be sufficient. Windmills cost about $700/m² of swept area. A CO₂ collection unit of 1 m² sweep area, with an extraction efficiency of 50%, and seeing an average wind velocity of 3 m/s would collect 3.6 kg of CO₂ per hour. Assuming a total annual cost for capital investment, operation, and maintenance of 30% of the cost of the machine, the collection cost is $5.70 per tonne of CO₂. At this point, the collected CO₂ is in the form of CaCO₃. Freeing the CO₂ again requires energy. Without accounting for inefficiencies, one would need ~0.15 t coal/t of CO₂. At a price of $20/t, the cost of this coal would add $3.00 to the tonne of CO₂. A rough estimate of the annual cost of the calcination plant is determined by multiplying the fuel cost by a factor of four. This is approximately the situation for a power plant. With these assumptions, the calcination process would add $12/t of CO₂ to the cost of the capture process. This cost would be tolerable compared to the cost of today's energy as well as compared to other sequestration efforts. For example, the cost of piping CO₂ a distance of 1,000 km has been estimated at ~$10/t of CO₂. For a coal-fired power plant at 33% conversion efficiency, $10/t of CO₂ translates into a little less than 1¢/kWh of electricity. Based on the relative carbon contents of coal and gasoline, the calcination required to collect the CO₂ from one liter of gasoline consumes about 0.7¢ worth of coal. Using the calculations performed above, the price of the complete process should be less than 5¢ per litre of gasoline, well within the range of recent price changes.

**Land Requirements.** Finally the size of the facilities to collect CO₂ or the required land area is considered. Imagine small collection units of some extent normal to the airflow, but of a height that is negligibe on the horizontal scale of the system. On the large scale, one may consider the surface of the horizontal area to be a good CO₂ absorber reducing the CO₂ density from an ambient value of $p_{CO₂}$ to (1 - ε)ρ_{CO₂}, where ε is the CO₂ removal efficiency. CO₂ is transported horizontally over the area by a wind velocity vₘ and it is transported vertically through eddy diffusion. The collection units near the surface remove CO₂ providing a gradient for vertical eddy diffusion transport. The observed eddy diffusion coefficient of the lower atmosphere is 10 m²/s. The vertical rate of mass transport is roughly ερ_{CO₂} (LΔv/L)^1/2, where L is the dimension of the collection area in the wind direction. Thus for an area of size LxW, the total rate of CO₂ removal is given by ερ_{CO₂} W(LΔv/L)^1/2. Assuming that L=W, ε=0.5 and vₘ=3 m/s, the land area required for collecting all CO₂ from a residential vehicle fleet of a city of 2 million is about 2.8 km on the side. A square, 530 km on the side, is sufficient to collect the CO₂ from all current anthropogenic sources. Since the rate of collection is proportional to L^1/2 rather than L, collection from several separate smaller areas would be more efficient than a single large area. If combined into a single area, these units will interfere with each other, with downwind units extracting CO₂ from already depleted air. If one were to limit the size of a collection unit to a square of 100 m on the side, then the world output of CO₂ would require 380,000 units, which is 1.4% of the area of a single collection system. Each of the latter units could consist of five vertical units, each 19 m tall by 19 m wide. Intuitive estimates indicate that the individual collection areas need to be spread over a total area as calculated above. Further spreading is not effective.

**Results and Discussion.**

We are performing global and high resolution atmospheric modeling and laboratory uptake experiments to further examine, quantify and develop CO₂ extraction from air as an advanced greenhouse gas separation and capture technology.

**Global Scale Modeling.** We have conducted large scale global simulations and sensitivity studies at 4° x 5° latitude/longitude resolution where a single grid-point land-based flat CO₂ sink is placed at various locations and with various deposition velocities (v)
in the UC Irvine Chemical Transport Model (CTM). The CTM contains nine vertical layers centered at 975, 909, 800, 645, 478, 328, 206, 112 and 40 mbar. The vertical resolution of the bottom layer is of order 1 km. This off-line code accepts wind fields from general circulation models and advects chemically interacting tracers and has been validated for many tropospheric applications. It allows us to assess the efficacy of global scale CO₂ extraction and identify locations that minimize impacts on downwind ecosystems that will experience reduced CO₂ levels and enhanced alkaline aerosols.

Figure 1 below shows the CTM’s sensitivity of the calculated amount of CO₂ extracted from the entire atmosphere as a function of time for a range of deposition velocities (v) at a single grid point surface sink centered in Nevada, USA. Observed deposition velocities for gases that react rapidly at terrestrial surfaces like SO₂ and HNO₃ are 1 and 4 cm/sec respectively. Our simulations indicate that extraction of the order of 10 Gtonnes-C/year is possible, even with a simple flat sink. These simulations also reveal the magnitude and extent of CO₂ depletion downwind of the sink that will be valuable to identify locations that minimize impact on terrestrial ecosystems. Saturation effects at high deposition velocities are caused by inability of mixing to replenish the sink box with more CO₂ from the rest of the atmosphere in this coarse CTM model.

High Resolution Modeling. The coarse global scale CTM modeling results presented above provide a lower limit to the CO₂ uptake flux per unit land area, as we illustrated earlier using scaling arguments in our land requirements section. Clearly we can improve our collection efficiency per unit of active land area by orders of magnitude by using smaller units with optimal spacing and designing structures that enhance turbulent mixing. We are using LANL’s high resolution and strong gradient (HIGRAD) code to quantitatively examine the detailed effects of mixing and turbulence on CO₂ collection. The code operates on a grid-point, finite-difference, compressible, and non-hydrostatic platform in terrain following coordinates with adaptive mesh capabilities. It uses a forward-in-time integration scheme that preserves local extremes and signs of transported properties. The parallel architecture allows it to harness our high-performance supercomputing platforms.

We are performing high-resolution simulations of air extraction of CO₂ using HIGRAD. The 2-Dimensional computations presented here have a horizontal resolution of 200 m and 63 vertical boxes with vertical grid being stretched gradually from 23 m at the surface to ~200 m at the top layer at 1.2 km. The velocity was set to 4 m/sec, and temperature of 300 K in an atmosphere with neutral buoyancy. The simulation used a steady stream of air with 370 ppm of CO₂ as its initial condition. The CO₂ concentrations were set to zero at the surface boundary to mimic an ideal flat sink that covers the entire horizontal domain. A parametric relation between the aerodynamic roughness and the friction velocity over water and similarity theory were used to treat the sub-grid fluxes and the vertical logarithmic wind profile above the surface. The results shown below in Figure 2, clearly reveal that CO₂ loss is observed hundreds of meters above the surface layer. Vertical mixing by turbulence is an effective source for CO₂ to the surface layer in a neutral atmosphere. Because we start with a uniform velocity profile, the turbulent velocity takes some time to get established as evident below. After this is achieved the real turbulent eddy structures become apparent for the conditions of our simulation.

Figure 2: Carbon dioxide concentration in ppm over a perfect aqueous sink simulated using HIGRAD. The distances are in meters above the surface and horizontally about a center of the domain.

Laboratory Experiments. We are performing controlled experiments of CO₂ uptake by saturated Ca(OH)₂ solutions in the laboratory. Ambient air is bubbled through a saturated Ca(OH)₂
solution with excess solid in an impinger. Care is taken to avoid evaporation by humidifying the input air stream. A metering pump is used to maintain stable flow that generates individual bubbles of a few mm in size that rise and remain intact in the solution. The amount of CaCO₃ formed at the end of a run (ranging from 15 minutes to 8 hours) is measured by titrating the mixture with acid and monitoring the pH. The inflection points of the pH curve yield the formation of Ca(OH)₂ particles. A LICOR CO₂ sensor is also being used to monitor the pH. The titration is done slowly and with rapid-stirring to ensure prompt dissolution of the fine CaCO₃ particles. A LICOR CO₂ sensor is also being used to provide a continuous measure of the CO₂ extracted from the air by bubbling.

The results from several CO₂ uptake experiments are summarized in Figure 3. There is close to a linear increase in CaCO₃ formed and CO₂ uptake with the volume of air processed. The contact time of the bubbles with the solution was varied by changing the height of the solution column. From the slopes of the above CaCO₃ formation data for 11 experiments we derive a mean CO₂ collection efficiency of 53 ± 5% from air by a saturated Ca(OH)₂ solution. The collection efficiency could be limited by kinetic factors such as CO₂ diffusion in the bubble and local in-homogeneity in the Ca(OH)₂ concentrations and pH of the solution in the vicinity of the bubble which will strongly influence the CO₂ uptake. However, an

Conclusions and Directions

Our economics and scaling arguments, atmospheric simulations, and laboratory experiments make a strong case to explore carbon-dioxide extraction from air as an advanced CO₂ capture and sequestration technology. By all measures we applied, this process compares very favorably against renewable sources such as solar, wind, or biomass. This scheme is attractive because; it allows CO₂ sequestration without a costly change in the existing infrastructure; it collects the CO₂ from the transportation and other distributed power sources; it retains carbon-based energy, which continues to be highly cost-effective, and it has the potential of restoring atmospheric CO₂ to pre-industrial levels providing us insurance against any large and rapid climate change events in the future. We are aggressively pursuing research on active and passive collection schemes, feasibility of CO₂ adsorbents like zeolites, silicates, amines, and Mg(OH)₂ with lower binding energy than CaCO₃, and identify locations that maximize collection, facilitate disposal, and minimize environmental impact. Our goal is to optimize the scale of the processes in order to design, construct, and develop a small prototype CO₂ extraction plant for field studies.

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References


Figure 3. Measurements of CaCO₃ formed as a function of the volume of ambient air (~370 ppm CO₂) bubbled through a saturated Ca(OH)₂ solution under controlled laboratory conditions.