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Thermal Removal of Carbon Dioxide from the Atmosphere: Energy Requirements and Scaling Issues

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Abstract

I conduct a systems-level study of direct air capture of CO_2 using techniques from thermal physics. This system relies on a combination of an efficient heat exchanger, radiative cooling, and refrigeration, all at industrial scale and operated in environments at low ambient temperatures. While technological developments will be required for such a system to operate efficiently, those developments rest on a long history of refrigeration expertise and technology, and they can be developed and tested at modest scale. I estimate that the energy required to remove CO_2 via this approach is comparable to direct air capture by other techniques. The most challenging aspect of building a system that could remove 1 billion tonnes of CO_2 from the atmosphere per year is the power demand of 112 to 420 GW during the wintertime operational period.

Introduction

Humanity's fossil fuel burning and land clearing have elevated atmospheric carbon dioxide (CO_2) from a preindustrial level of approximately 280 (Joos and Spahni 2008) parts-per-million by volume (ppmv) to above 400 ppmv (IPCC 2014). Because CO_2 readily admits the Sun's visible light, yet selectively absorbs infrared light reradiated from the Earth, its increased abundance warms and modifies the Earth's climate. Enhanced atmospheric CO_2 also increases dissolved CO_2 in the oceans, increasing their acidity, which threatens coral reefs and many marine species (Frieler et al. 2013; Gattuso et al. 2015). Anthropogenic methane, other gases, aerosols, and soot also contribute to climate change, yet it is CO_2 that currently plays the largest role in modifying Earth's climate (Strassmann, Plattner, and Joos 2009). While the global community is beginning to reduce humanity's fossil fuel use, even aggressive moves to renewables, nuclear power, and higher efficiency will still drive the atmospheric and oceanic CO_2 load substantially higher. For instance, under the 2015 Paris Agreement, nations pledged CO_2 emission rate reductions until 2030, and have less than 15 years to achieve zero net carbon emissions (Framework Convention on Climate Change, 2016; Schleussner et al. 2016). Yet without further, stricter commitments, realistic assumptions based on the 2015 Paris Agreement still yield atmospheric CO_2 above 450 ppmv. There is a strong case that 450 ppmv CO_2 is too high, and in fact the safe CO_2 level may be closer to 350 ppmv (Hansen et al. 2008). The scenarios modeled by the Intergovernmental Panel on Climate Change (IPCC 2014) assume an additional 990 to 6180 billion metric tons (Gt) of CO_2 emissions by 2100 (Collins et al. 2013). Because natural weathering processes require thousands of years (Archer et al. 2009), all of Earth's inhabitants will have to cope with this excess CO_2 for many centuries unless humanity finds a means to remove CO_2 from the atmosphere (Lackner et al. 2012).

A number of research groups are working on approaches to removing CO_2 from the atmosphere. This research, if successful, would provide a societal insurance policy, yielding relief if humanity exceeds safe CO_2 levels. Additionally, this research provides a method of calculating the market cost of CO_2 emission. Direct air capture of CO_2 via adsorption-based and chemical-based approaches (Stolaroff, Keith, and Lowry 2008; Keith, Heidel, and Cherry 2009; Lackner et al. 2012) are being developed, yet considerable research is required in order to determine how well and at what cost these approaches scale to the multi-Gt level. A fundamentally different, thermal physics approach has also been suggested (Agee, Orton, and

Rogers 2013). The thermal approach takes advantage of the fact that CO_2 has the highest phase transition temperature of the atmospheric gases, with the exception of water. Yet water is easy to handle and can be largely avoided in cold environments. Agee, Orton, and Rogers (2013) present a theoretical description of a system meant to achieve direct air capture of CO_2 by cooling Antarctic air to the point where CO_2 desublimates out of the atmosphere. They also propose burying CO_2 in insulated landfills within the Antarctic icefield. A related thermal approach has been developed to capture CO_2 from power plant exhaust streams (Clodic and Younes 2002; Baxter, Baxter, and Burt 2009; Tuinier et al. 2010). While the latter technology provides useful guidance for direct air capture, it operates at higher CO_2 concentration (14% versus 0.04%), higher intake temperature (150 °C), and much lower ($\sim 10^{-3}$) volume flow rates. This means that a system designed to capture CO_2 from power plant exhaust cannot readily be scaled to direct air capture.

The calculations I present below show that a thermal approach could remove CO_2 from the atmosphere for an energy cost of just over 1 GJ per metric ton (hereafter written as tonne), which is similar to the energy costs for chemical-based techniques (Keith, Ha-Duong, and Stolaroff 2006; Stolaroff, Keith, and Lowry 2008). As reference numbers, this paper focuses on removing either 100 or 1000 Gt of CO_2 from the atmosphere over a 100-year period.

In what follows, I develop a systems-level theoretical framework, including the energy requirements and an initial assessment of the quantity of materials required for a thermal method of direct carbon capture from air, which I refer to as direct cryogenic carbon capture (DCCC). This paper does not focus on how to render so much CO_2 into a benign state or where to store it, which is the goal of carbon sequestration. There is hope that accelerating natural weathering (Kelemen and Matter 2008; Matter and Kelemen 2009) will be practical and that CO_2 can be converted to relatively benign stable carbonate rocks. This paper focuses instead on how to directly remove CO_2 from the atmosphere (i.e., carbon capture).

Thermal Approach: Cool and Rewarm Air at Near-Ambient Pressure

In this calculation, I explore the energy required to cool air to the point where CO_2 desublimates out as dry ice, then rewarm the air back to the ambient temperature via an efficient heat exchanger. This system also takes advantage of cooling via radiative coupling with a wintertime night sky as well as being sited in a naturally cold environment. Figure 1 presents the block diagram for the system. In this figure, ambient air enters at the bottom right, is cooled through a precooler stage, then enters a CO_2 deposition chamber (in the middle of the figure) where additional cooling takes place. That additional cooling is performed by a cryogenic refrigeration cycle, presented at the top of the figure. After CO_2 deposition, the bulk of the air is cycled back through the precooler (lower left flow), where it absorbs thermal energy from the incoming ambient air. The precooler is composed of two functional components: a heat exchanger to pass heat from the ingested ambient air to the cold air exiting the CO_2 deposition chamber and a radiative cooler to further remove heat from the ingested air.

The equation describing this process is

$$EC = \frac{(|Q_{air}|(1 - e_{air}) + |Q_{CO2}|(1 - e_{CO2}) - |Q_{rad}|g)}{COP} + \frac{G_{sep}}{\eta} + E_{HE}, \qquad (Eq\ 1)$$

where EC is the energy cost in Joules of separating CO_2 from 1 m^3 of air; $|Q_{air}|$ and $|Q_{CO2}|$ are the heat removed from the volume of air and CO_2, respectively; e_{air} and e_{CO2} are the fractional recovery of Q_{air} and Q_{CO2} by the heat exchanger, respectively; $|Q_{rad}|$ represents radiative cooling; g is a guillotine factor, which is 1 above the radiative cooling temperature and 0 below; COP is the coefficient of performance for the refrigeration system; G_{sep} is the Gibbs free energy associated with the entropy change of separating CO_2

from air; η is the efficiency of the refrigeration system during CO_2 desublimation; and E_{HE} is the energy needed to move 1 m^3 of air through the heat exchanger and CO_2 deposition chamber.
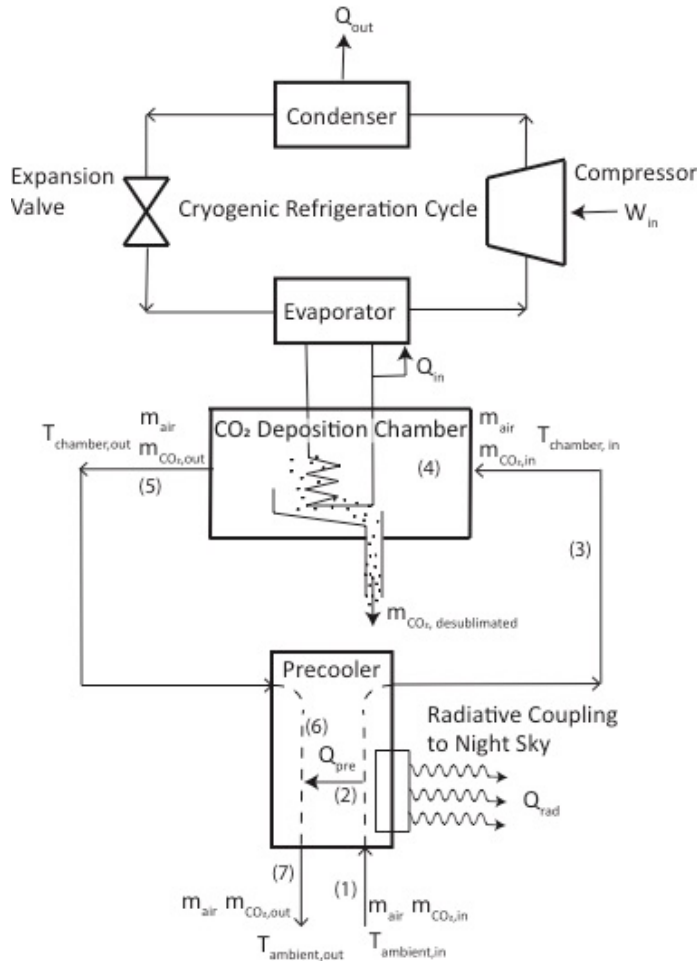
Fig. 1: Block diagram for the proposed DCCC system. Ambient air enters at (1) near the bottom right, is cooled through (2) a pre-cooler stage, then (3) enters a (4) CO_2 deposition chamber (in the middle of the figure) where additional cooling takes place. That additional cooling is performed by a cryogenic refrigeration cycle, presented at the top of the figure. After CO_2 deposition, the (5) bulk of the air is cycled (6) back through the precooler (lower left flow), where it absorbs thermal energy from the incoming ambient air before (7) being exhausted. The precooler is composed of two functional components: a heat exchanger to pass heat from the ingested ambient air to the cold air exiting the CO_2 deposition chamber and a radiative cooler to further remove heat from the ingested air.

Q_{air} is the dominant term in Eq. 1. To keep energy costs as low as possible, it is important to operate the DCCC system in a cold environment. As example environments, I chose locations with ambient temperatures of –20, –40, and –65 °C. The first environment is common in much of northern Canada in the winter, and is the average temperature for Snag, Yukon during November through February[1]. The second environment is the average temperature in Oymyakon, Russia from November through February[2]. The third environment is the average temperature for the Vostok Station, Antarctica from April through September[3].

It is possible that a DCCC system would not use separated, cooled CO_2 as a heat exchanging fluid, both because of the extra exchanger pathways that would be needed and because solid CO_2 may have commercial value during the technology development stage (Sipöcz et al. 2013). For this reason, e_{air} and e_{CO2} are treated separately. In the case where CO_2 is not routed back through its own heat exchanging path, $e_{CO2} = 0$ and the combination of radiative cooling and refrigeration pay the full energy cost of Q_{CO2}, rather than the fractional $(1 - e_{CO2})$ cost that a heat exchanger allows.

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[1] en.wikipedia.org/wiki/Snag,_Yukon

[2] en.wikipedia.org/wiki/Oymyakon

[3] en.wikipedia.org/wiki/Vostok_Station

The relationship among heat, Q, a change in temperature ΔT for a mass of substance, m, depends on the specific heat, c, and latent heat, L, according to the well-known equation $Q = m \, c \, \Delta T + m \, L$. For a system operating at constant pressure, which is sufficiently accurate for this calculation, $Q_{air} = m_{air} \, c_p(air) \, \Delta T + m_{H2O} \, L_{H2O}$ and $Q_{CO2} = m_{CO2} \, c_p(CO_2) \, \Delta T + m_{CO2} \, L_{CO2}$. The latent heat term for water would not be multiplied by the heat exchanger term if any gas phase water in the incoming air were impractical to return to the gas phase in the rewarming air. This could happen if the ambient air contains super-cooled water vapor that would freeze in the heat exchanger intake path but not be rewarmed sufficiently to sublimate in the heat exchanger exhaust path. This term, which is included in subsequent calculations, is anyway small, because a DCCC system would operate under conditions cold enough that ambient air is already well below the freezing point of water. Thus, ingested air would be very dry.

Radiative coupling to the night sky, Q_{rad}, may help achieve additional cooling. The night sky has a non-thermal spectrum dominated by H_2O and CO_2 emission. For example, infrared spectra of the sky over Barrow, Alaska show emission with a brightness temperature of ~245 K between 13 and 17 μm yet as little as ~160 K at other wavelengths (Marty et al. 2003; Petty 2008). The night sky spectrum over Antarctica is qualitatively similar and even colder (Walden, Warren, and Murcray 1998). Tests at a mid-latitude site (Chen et al. 2016) show that a simple blackbody thermal radiator can reach an equilibrium temperature approximately 20 °C cooler than its environment, while an advanced thermal radiator coupled to the atmospheric transparency window of 8 to 13 μm can maintain an average equilibrium temperature 37 °C cooler than its environment. The equilibrium temperature is, however, not the appropriate operating temperature because at that point $Q_{rad} = 0$. Assuming instead that the radiative temperature is set at 20 °C below the ambient temperature, the power radiated is approximately 30 W/m^2 for the advanced radiator (Chen et al. 2016). These numbers are appropriate to a mid-latitude site. At the cold sites envisioned here there will be roughly offsetting effects on Q_{rad}: decreasing because the radiative temperature is lower, increasing because the atmospheric window is more transparent and covers a wider range of wavelengths at these sites. I will assume that these effects approximately cancel out. For a reference air flow of 1 m^3/s through a DCCC system, radiative cooling with a 10 m^2 radiator is sufficient to cool the ambient air by 20 °C when passed through a heat exchanger with $e_{air} = 0.99$.

The entropy of mixing a trace species into a large volume is given by the equation

$$S_{mix} = -n \, R \, (x_1 \ln x_1 + x_2 \ln x_2), \qquad\qquad (Eq\ 2)$$

where the molar density of air, n = 48.14 moles/m^3 at T = –20 °C, and x_i is the mole fraction of component i. At 405 ppmv[4] CO_2, $x_i = 4.05 \times 10^{-4}$ and S_{mix} = 1.254 J/K per m^3. The Gibbs free energy change associated with undoing this mixing entropy is

$$G_{sep} = -G_{mix} = T \, S_{mix}, \qquad\qquad (Eq\ 3)$$

which is 260.9 J/m^3 at –65 °C and 317.3 J/m^3 at –20 °C. These numbers are appropriate for a system that returns CO_2 to the ambient temperatures of the Yukon and Antarctic sites, respectively. G_{sep} also sets the lower limit to the energy cost that the system can achieve. The value of 260.9 J/m^3 is equivalent to 10.2 kJ/mole CO_2 or 351.8 MJ/tonne CO_2 removed. This is consistent with a value of 509 MJ/tonne CO_2 derived in a study of removing CO_2 from flue gas or ambient air at somewhat higher temperature (Budzianowski 2017).

The theoretically best *COP* is that of the Carnot Cycle, with $COP_{Carnot} = T_{cold} / (T_{hot} - T_{cold})$. The currently achievable *COP* values for cryogenic refrigeration systems at these temperatures are $\eta = COP/COP_{Carnot}$

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[4] www.esrl.noaa.gov/gmd/obop/brw/

≈ 0.15 (Hugh, Mathison, and Bowman 2013; Song, Kitamura, and Jiang 2013). This leaves substantial room for improvement in the *COP* of a system designed for this purpose. The advantage of using η instead of *COP* is that η is independent of the change in temperature and it is also relevant to the G_{sep} term of Eq. 1. For the calculations of this paper, I use η = 0.15, 0.3, and 0.5 and assume that η has the same value above the CO_2 desublimation point and within this temperature regime.

To calculate E_{HE}, I use the Zehnder ComfoAir 350™[5] as a guide. This system's maximum efficiency setting equates to E_{HE} = 610 J/m^3. This commercial system is specified over a range of $\Delta T \geq 26.5$ °C and $T_{cold}/T_{hot} \approx 0.91$. This is less than required in a DCCC system with ΔT = 65 to 110 °C and T_{cold}/T_{hot} = 0.53 to 0.65. I scale the above E_{HE} value by these temperature ratios, and round to E_{HE} = 940 J/m^3. Work done on the gas scales as $1 - T_{cold}/T_{hot}$, and therefore the above scaling approximates both the back-pressure of the air flow and work done on the gas due to temperature changes causing pressure and volume changes. I also calculate E_{HE} based on a prototype heat exchanger (Koplow 2010) that drives down E_{HE} by a factor of five.

The fraction of CO_2 actually removed during desublimation, f_{CO2}, depends on T_{cold}. Because CO_2 vapor pressure drops as more CO_2 is desublimated, decreasing temperatures are needed to achieve higher removal fractions. (An inefficient system could also lose already separated CO_2, but I assume this is not happening appreciably.) Fitting available data (Bryson, Cazcarra, and Levenson 1974; en.wikipedia.org/ wiki/Carbon_dioxide_(data_page)), I find that T_{cold} = –139.6, –142.7, –150.0, and –160.4 °C for initial desublimation, 50% drawdown, 90% drawdown, and 99% drawdown, respectively. These temperatures are consistent with experimental results (Agee and Orton 2016) within a few degrees, and sufficiently accurate for this calculation. While higher values of f_{CO2} are preferable from the standpoint of decreasing *EC*, this requires lower values of T_{cold}, which increases energy costs. There is therefore a trade-off between a greater CO_2 removal fraction and the requirement for lower cold-side operating temperatures (T_{cold}) that depends only weakly on the intake air temperature (T_{hot}) and which may affect cooling efficiencies (η). I perform a preliminary analysis of this trade-off and find a minimum energy expenditure close to T_{cold} = –150 °C, with f_{CO2} = 90%. The value for T_{cold} varies by only a degree or two as a function of T_{hot}, so T_{cold} = –150 °C will be used in the remainder of this analysis. I do not include f_{CO2} in Eq. 1 because it only affects Q_{CO2} and G_{sep}, and for any reasonably high value of f_{CO2} this will have minimal practical consequences on the energy cost of operation, *EC*.

Figure 2 presents *EC*, the energy cost of removing CO_2 from the atmosphere in GJ/t, as a function of *dT*, the temperature difference between the warm and cold air streams in the heat exchanger. *EC* values are presented for three levels of refrigeration performance, η, and two values for the energy required to move air through the system, E_{HE}. The values of η match those that are currently achievable (η = 0.15) and potential available after development (η = 0.30 and 0.50). The values of E_{HE} match those that are currently achievable (E_{HE} = 940) and expected from prototype technology (E_{HE} = 188 J/m^3; Koplow 2010), as discussed above. This analysis is valid for any of the four modeled operating conditions: (1) without radiative cooling in an environment where the ambient air temperature is –20 °C, (2) with 20 °C radiative cooling in an environment where the ambient air temperature is –20 °C, (3) –40 °C, and (4) –65 °C. To compensate for these different values of ambient temperature, the efficiency of the heat exchanger (e_{air}) is adjusted in order to yield the same temperature difference, *dT,* between the warm and cold air streams at the cool end of the heat exchanger. The grey band running across the bottom of Figure 2 indicates the estimated range of energy required to operate chemical-based direct air capture at 1.20 to 1.73 GJ/t (Stolaroff, Keith, and Lowry 2008).

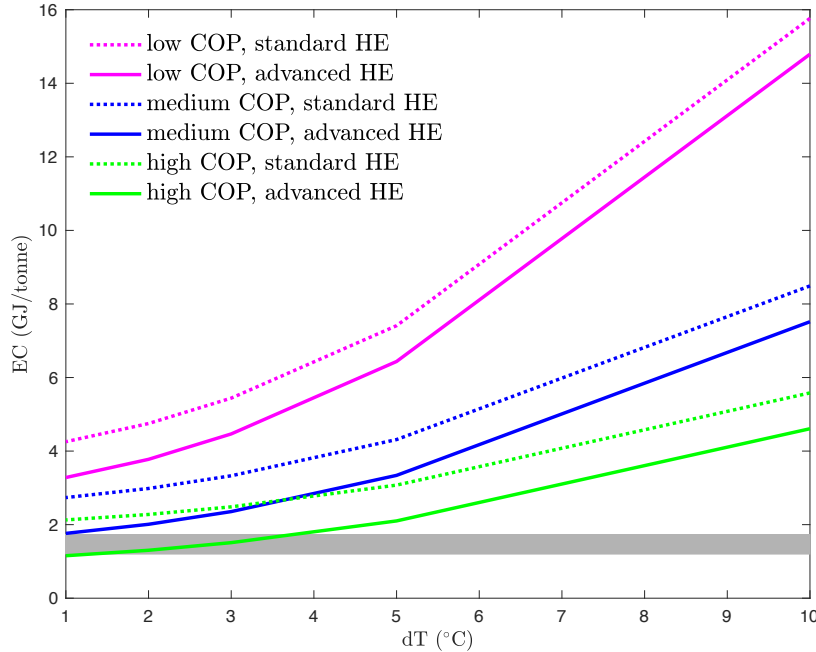[5] zehnderamerica.com/wp-content/uploads/2014/11/CA350-2015.03.25.pdf

Fig 2: EC, the energy cost of removing CO_2 from the atmosphere in GJ/t, as a function of dT, the temperature difference between the warm and cold air streams in the heat exchanger. EC values are presented for three levels of refrigeration performance (low, medium, and high values of COP, corresponding to $\eta = 0.15$, 0.30, and 0.50, respectively) and two values for the energy required to move air through the system ($E_{HE} = 940$ and 188 J/m^3).

Figure 2 indicates that a DCCC system may require approximately the same energy to operate as chemical-based direct air capture if dT can be held to ≤ 3 °C and if cryogenic refrigeration can be pushed to higher efficiency ($\eta > 0.3$). Keeping $dT \leq 3$ °C is realistic at the Antarctic site, where for these dT values $e_{air} = 0.954$ to 0.985. These dT values are more difficult at the Yukon site, yet should be possible even without radiative cooling, requiring $e_{air} = 0.977$ to 0.992. Higher η values would significantly help the DCCC approach and may, in turn, be facilitated by the small temperature range, also equal to dT, over which this refrigeration cycle operates.

Considerations to Bring a DCCC System to Scale

Heat Exchanger Component

As a starting point to estimate the heat exchanger component size and mass of a DCCC system, I used an on-line calculator for a commercial tube counter-flow heat exchanger[6] and tuned the flow rate to achieve 99% fractional recovery of Q_{air} ($e_{air} = 0.99$). I scaled this system from its stainless-steel design to aluminum, to the temperature range needed, and conservatively decreased its mass to operate at a pressure of one atmosphere from its design specification of 28 bars. The resulting 1 m^3 aluminum counter-flow heat exchanger would have a mass of 252 kg and an air flow rate of 1.53 kg/s or 1.1 m^3/s when operating at e_{air} = 0.99. This value is slightly higher than needed for $dT = 2$ °C and $\eta = 0.15$ at the Yukon site (which would require $e_{air} = 0.985$), so serves as an upper limit to the heat exchanger mass. The heat exchanger mass scales linearly with $1 - e_{air}$. At the coldest site and if $\eta = 0.5$ refrigeration is practical, then $e_{air} = 0.846$ may be sufficient and the heat exchanger mass drops to only 16.4 kg per m^3 package. Limiting consideration to $\eta = 0.15$ refrigeration, the Antarctic site requires $e_{air} = 0.954$, or 54.8 kg of heat exchanger material in a 1 m^3 package to handle the same air flow rate. From these Yukon and Antarctic limiting cases, I use heat exchanger masses of 250 kg and 55 kg for an airflow rate of 1.53 kg/s.

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[6] calc.exergyllc.com

Assuming a system scaled to draw 100 Gt CO_2 out of the atmosphere over 100 years and assuming the system operates for the 120 coldest days of the year with an 80% duty cycle times desublimation fraction ($f_{duty}f_{CO2}$ = 0.8), then the system must process 0.14 km^3/s of air. This requires a heat exchanger volume of 0.13 km^3. An Antarctic site may operate 180 or more days per year, reducing the air processing rate to ≤ 0.09 km^3/s. Processing this air through the decreased temperature range of 65 °C requires a heat exchanger volume of order 0.02 km^3. The total heat exchanger mass for the 1 Gt/yr system is 32 or 5 million tonnes in the Yukon or Antarctic cases, which would put substantial demand on the world aluminum market, which in 2016 was 58.9 million tonnes[7]. The heat exchanger would require 54% or 9% of the world's one-year production of aluminum and may drive up aluminum prices even if built over 10 to 20 years. Although the heat exchanger is unlikely to last 100 years, the bulk of the material could be recycled, so these materials are procured only once. A 1000 Gt scaled system would require ten times as much material, which would severely stress the world aluminum market for a DCCC system entirely located in the Yukon.

These above calculations conservatively assume that billions of dollars invested in heat exchangers would not substantially improve their performance as a function of mass. Because the heat exchanger would operate at atmospheric pressure, thinner conducting surfaces with less mass and material cost could most likely be used. Additionally, the fundamental limit in air-to-air heat exchangers is currently set by the insulating properties of the nearly stationary boundary air at the air-conductor interface. A prototype system that removes much of the boundary layer has been developed (Koplow 2010). It appears that this approach could drive down system mass by at least a factor of four. Thus, there are reasons to be optimistic that the volume and mass of the DCCC heat exchanger could be a factor of 5 to 10 less than the above estimate.

Passive Radiator Component

Above, I calculated that a radiator with a surface area of 10 m^2 would provide 20 °C of cooling for an airflow of 1 m^3/s for a heat exchanger with e_{air} = 0.99. For a system scaled to airflow of 0.14 or 0.09 km^3/s, this corresponds to a radiative cooling area of 1400 or 900 km^2. Radiators of this scale argue for modular DCCC systems distributed over at least this land area. If made from 1 mm-thick aluminum, the total aluminum needed would be 3.78 million or 2.52 million tonnes, which is substantially less material mass than the heat exchanger component.

Refrigeration Component

Assuming a DCCC system could be built that had an energy cost of 2.0 (Antarctic site) or 5.0 GJ/t (Yukon site) of CO_2 removed from the atmosphere, then drawing 100 Gt CO_2 out of the atmosphere over 100 years, under the assumptions outlined above, dictates a power demand ranging from 160 GW (Antarctica site) to 600 GW (Yukon site). For combinations of η, E_{HE}, and location, that power demand varies from 98% refrigeration and 2% air handling to 43% refrigeration and 57% air handling. As a representative case, I apportion the power demand as 70% refrigeration and 30% air handling and look at the implications for refrigeration scaled to 420 GW for 120 days per year (Yukon site) or 112 GW for 180 days per year (Antarctic site). The total energy demands in these two cases are approximately 4400 PJ or 1200 PJ. By way of comparison, the worldwide yearly residential air conditioning demand is approximately 2500 PJ and is expected to reach 5000 PJ in the late 2020's (Isaac and van Vuuren 2009), so a DCCC system scaled to 420 GW would be comparable to the world's total supply of residential air conditioning in a decade.

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[7] www.world-aluminium.org/statistics/#data

Power Requirement

The total power requirement of 600 GW or even 160 GW is challenging. For comparison, the world's largest nuclear power plant is Japan's 8 GW Kashiwazaki-Kariwa facility, the largest wind farm, Gansu in China, is slated to reach 20 GW by 2020[8], and the entire United States uses electricity at an average rate of 450 GW[9]. Yet this problem may be somewhat less overwhelming than it initially appears. For the representative 70/30 split between refrigeration and air handling, much of the air handling could be delivered by on-site wind technology. The DCCC system discussed above moves air at only 1 m/s through the heat exchanger, whereas the average wind speed at Vostok Station[10] is 5 m/s. Other Antarctic sites are substantially windier (Parish and Bromwich 1987; Agee, Orton, and Rogers 2013). Local winds could power the airflow and even provide a fraction of the power for refrigeration. Of the 112 to 420 GW of cooling, note that this power is needed only during the coldest months. For the remainder of the year, whatever fraction of this power was generated year-round at no additional cost (e.g. by wind) could be available to the surrounding areas, which would add economic return from a DCCC system. Nevertheless, power demands are clearly substantial and may limit DCCC system drawdown to less than 1 Gt/yr.

Further Considerations

In the limit where E_{HE} is powered by local winds and where the entropy term, G_{sep}, is small, a 1 degree decrease in $T_{hot} - T_{cold}$ yields a 1.8% drop in EC, while a 1 degree increase in T_{cold} yields a 2.6% drop in EC. One can decrease T_{hot} by operating in a colder environment, with more radiative cooling, or with a more efficient heat exchanger. One can increase T_{cold} by operating the system at a higher cold-side temperature, which either would entail desublimating a lower fraction of CO_2 (decreasing f_{CO2}) or would require raising the desublimation temperature of CO_2. The latter may be possible using surface catalytic chemistry (Pandey et al. 2016) or electric charges (Ehre et al. 2010), at least by a few degrees. Additionally, if the refrigeration efficiency, η, can be tuned to a maximum near the CO_2 desublimation temperature, the entropy contribution can be minimized.

Throughout the analyses above, I assumed that the input air contains 405 ppmv CO_2. If a technology could be developed that cheaply pre-concentrates CO_2 to a higher partial fraction, and assuming that the entropy term, G_{sep}, does not dominate energy costs, then the energy and refrigeration costs would be reduced by this pre-concentration ratio. This is not an argument to wait until anthropogenic emissions increase CO_2 even further, because the system size depends on how many years are available to draw down atmospheric CO_2 and because, if atmospheric CO_2 is already too high (Hansen et al. 2008), it must be reduced to less than 405 ppmv anyway. It is also not an argument to feed concentrated CO_2 streams from power plants or natural sources into a DCCC system, because capturing carbon at these sources would be cheaper and easier before those streams are diluted.

Conclusions

A well-designed and located DCCC system may be capable of removing CO_2 from the atmosphere with an energy requirement comparable to chemistry-based techniques (Keith, Ha-Duong, and Stolaroff 2006; Stolaroff, Keith, and Lowry 2008). The most challenging aspect of building a system that could remove 1 Gt/yr of CO_2 from the atmosphere is the power demand of 112 to 420 GW during the winter-time operational period. Research developments in heat exchangers, radiative cooling, and refrigeration all have the potential to lower overall costs and this large power requirement.

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[8] en.wikipedia.org/wiki/List_of_largest_power_stations
[9] www.cia.gov/library/publications/the-world-factbook/rankorder/2233rank.html
[10] en.wikipedia.org/wiki/Vostok_Station

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