Proposal for direct air capture of CO₂ during the Antarctic winter using physisorption

Clifford W. Hicks¹,²

¹School of Physics and Astronomy, University of Birmingham, Birmingham B15 2TT, United Kingdom
²Max Planck Institute for Chemical Physics of Solids, Nöthnitzer Str. 40, 01187 Dresden, Germany

The possibility of direct air capture of CO₂ in Antarctica is discussed. Because the concentration of H₂O in the atmosphere during the Antarctic winter is extremely low, an installation for direct air capture could employ a physisorption-based process, allowing, in principle, a very short adsorption/desorption cycle time. The lower required binding allows more options for materials for the sorbent. With a shorter cycle time, more resource could be spent on structuring the sorbent to improve energy efficiency, for example by improving its mass efficiency if desorption is driven thermally.

1. Introduction. At present humanity emits ≈ 35 Gt/y (gigatonnes per year) of CO₂ [1]. Direct capture of CO₂ from the environment is likely to become a necessary component of climate change mitigation [2,3]. The companies Climeworks [4] and Carbon Engineering [5], for example, are pursuing direct air capture (DAC) of CO₂ through installations built for this purpose. The required area for these installations is much less than that required for biochar or enhanced weathering, other possible methods for CO₂ capture. However, the energy requirement is vast. Both companies employ adsorption/desorption cycle to capture CO₂. Carbon Engineering’s process uses a KOH sorbent, and is calculated to consume 390 kJ per mole of captured CO₂ (4.0 eV per CO₂ molecule) [5]. Climeworks’ process employs amine scrubbing, and also requires, as of 2015, ≈ 400 kJ/mol [6,7]. Scaled up to a capture rate of 10 Gt/y, 4 eV per molecule equates to 9 · 10¹⁹ J/y, roughly matching the primary energy consumption of the United States. Energy efficiency is critical for implementing DAC at scale.

This article explores the possibility of performing DAC in Antarctica. Its central premise is that a physisorption-based process can be employed. Physisorption is adsorption through interaction with the electrical properties of the adsorbate molecules: van der Waals and electrostatic interactions. In the CO₂ molecule, the oxygen atoms are negatively charged and the carbon positively charged, so CO₂ molecules adhere to charged surfaces more strongly than the other major components of the atmosphere, except H₂O. H₂O, having a strong electric dipole moment, usually adheres to charged surfaces even more strongly. Therefore, to obtain CO₂ rather than H₂O, adsorption processes operated in temperate climates must typically use chemisorption, which is adsorption involving exchange of an electron and which offers chemical selectivity [8,10].

During the Antarctic winter the concentration of H₂O in the atmosphere is low enough that chemical selectivity might not be necessary. For pure physisorption there is no activation energy. In addition, during the Antarctic winter there will be no fluid layer on the sorbent surface through which CO₂ must diffuse [3]. Therefore, the cycle time can in principle be very short. A short cycle time, in turn, would allow more resource to be spent on structuring the sorbent, which in turn could yield substantial improvement in energy efficiency. For example, if desorption is driven by heating, then energy efficiency is improved by making the sorbent as light as possible relative to its capacity to adsorb CO₂.

There are three further advantages to operation in Antarctica. One is the reliability of the katabatic winds, a potential power source. The second is that the high plateau of the Antarctic ice sheet is empty; there are no competing land uses, and the penguins live on the coast. The third is that captured CO₂ could be stored by injection into the ice sheet.

The following sections are: (2) The capture cycle and energy consumption are summarised. (3) A conceptual sorbent structure suitable for a 1 s cycle time is presented. 1 s is chosen as an illustration what may be possible, not as a carefully-considered optimum. (4) The optimum adsorption binding energy is calculated. (5) The energy cost of purge cycles to remove H₂O is discussed. (6) The katabatic winds and (7) storage of captured CO₂ are discussed.

2. Operating conditions and the capture cycle.

The capture installations are presumed to operate on the high plateau of the east Antarctic ice sheet, at an elevation of around 3500 m, where the ambient pressure is ≈ 65 kPa. The average winter temperature is below −60°C (213 K), and can drop to −90°C [11]. An ambient CO₂ concentration of 400 ppm is assumed.

The capture cycle is summarised in Table I. A maximum operating temperature for the capture machinery

| TABLE I. The capture cycle. |
|-----------------------------|
| 1. Adsorb CO₂ at T ≤ −58°C, P ≈ 65 kPa. |
| 2. Desorb CO₂ at T ≈ 100°C, P = 1.3 kPa. |
| 3. Compress the CO₂ to ~ 10 MPa, while allowing it to cool to −40°C. |
| 4. Inject the CO₂ into the ice sheet. |
of $-58^\circ$ C is selected, allowing it to operate for slightly more than half of the year [11]. This limit is due to the presence of H$_2$O in the atmosphere. CO$_2$ is adsorbed at ambient conditions, and then is desorbed by reducing the pressure and heating the sorbent to $\approx 100^\circ$ C. The pressure reduction reduces the amount of heating required, and so also the energy consumption for desorption [6, 7]. In step 3, the CO$_2$ is then compressed to $\approx 10$ MPa, and as it is compressed heat sinks allow it to cool to $\approx -40^\circ$ C. The CO$_2$ will liquify. For storage, it can then be injected into the ice sheet: at a pressure of 10 MPa it can be injected to a depth of 1 km.

Table II lists the components of the energy consumption that will be discussed. These figures assume a sorbent capacity of 10 wt % CO$_2$, meaning that the mass of CO$_2$ captured when every binding site is occupied is 10% of the mass of the empty sorbent.

3. Illustrative sorbent structure. To obtain an illustrative cycle time of 1 s, which is 3–4 orders of magnitude faster than typical [9], I suppose that the adsorption and desorption times will each be $\sim 0.3$ s, leaving $\sim 0.4$ s to carry out the temperature and pressure changes. In reality, the optimum cycle time will be set by a balance between the economic cost of the sorbent, which favours a short cycle time, and limits on the mechanical engineering required to drive the temperature and pressure swing, which will almost certainly favour a longer cycle time. This is because, for energy efficiency, the amount of material that undergoes cyclic heating must be kept to a minimum. The rate at which CO$_2$ can be delivered to the sorbent is essentially fixed by the energy budget for driving the flow through the sorbent, so the amount of CO$_2$ that could be captured in each cycle is proportional to the cycle time, $t_{cycle}$. The depth that heat penetrates into surfaces is proportional to $\sqrt{t_{cycle}}$, so the energy cost of cyclic heating per captured CO$_2$ molecule will in general be proportional to $1/\sqrt{t_{cycle}}$; smaller for longer $t_{cycle}$. As illustrated in the conceptual sorbent structure shown in Fig. 1, if the sorbent support structure is conductive then heating could be accomplished by running current through the sorbent; it is nevertheless inevitable that some of the applied heat will spread beyond the sorbent.

To minimise conduction of heat beyond the sorbent, it will be advantageous to hold the sorbent with thermally insulating supports. That would mean that the heat of adsorption dissipates into the airflow. This is acceptable. It will be shown below that the optimum adsorption binding energy is $\sim 0.4$ eV, so the temperature of the airflow rises by:

$$\Delta T = \frac{0.4 \text{ eV} \times 4 \cdot 10^{-4}}{\frac{1}{2}k_B} = 0.7 \text{ K.}$$

In our illustrative structure (Fig. 1), the sorption sites are inside pores of diameter $d_{pore}$ and length $l_{pore}$. The pores are on the inside of larger tubes, of inner diameter $d_{tube}$ and length $l_{tube}$, through which air is flushed.

The Reynolds number for flow through a tube is $Re = \rho v d_{tube}/\mu$, where $\rho$ is the density of the air, $v$ the average flow velocity through the tube, and $\mu$ the dynamic viscosity of the air. At 65 kPa and 213 K, $\rho \approx 1.1 \text{ kg/m}^3$, $\mu \approx 1.4 \cdot 10^{-5} \text{ kg/m-s at 213 K}$ [12], and I select $d_{tube} = 50 \mu$m. Setting $v = 6 \text{ m/s}$, as indicated in Fig. 1, yields $Re \approx 25$, so laminar flow is expected [13]. For laminar flow through a tube [13],

$$v = \frac{\Delta P d_{tube}^2}{32 l_{tube} \mu},$$

where $\Delta P$ is the pressure differential across the tube.

In setting the tube dimensions, we require that CO$_2$ molecules be able to diffuse across the tube diameter in the time that the flow transits the tube. At time $t'$, the typical diffusion velocity is $v_{diff} = \sqrt{D/t'}$, where $D$ is

![Fig. 1. Conceptual sorbent structure for an adsorption time of $\sim 0.3$ s. It consists of a set of tubes of diameter $d_{tube} = 50 \mu$m through which air passes, lined with pores of diameter $d_{pore} = 40 \text{ nm}$ and depth $l_{pore} = 2 \mu$m. The tube shells may be conductive, so that the sorbent could be heated by applying current.](Image)
the diffusion constant of CO₂ in air at 65 kPa and \( T \approx 200 \text{ K} \). The average diffusion flow between \( t' = 0 \) and \( t' = t \) is \( \langle v_{\text{diff}} \rangle = 2\sqrt{D/t} \). The condition that molecules have time to diffuse across the tube diameter corresponds to \( \langle v_{\text{diff}} \rangle = v_{\text{tube}}/l_{\text{tube}} \). Setting \( t \) to the transit time, 
\[
v = \frac{4l_{\text{tube}}D}{d_{\text{tube}}^2}.
\]
Combining Eqs. 1 and 2 yields:
\[
v = \sqrt{\frac{D\Delta P}{8\mu}}.
\]
\( \Delta P \) is obtained by selecting the power consumption for driving the flow. If this power consumption is set at 0.4 eV per captured CO₂ molecule, the fans driving the flow are 50% efficient, and the total capture efficiency for CO₂ passing through the device is 75% (Carbon Engineering’s target [5]), then \( \Delta P = 200 \text{ Pa} \). \( D \approx 1.2 \cdot 10^{-5} \text{ m}^2/\text{s} \) [12], yielding \( v = 6 \text{ m/s} \). For comparison, the inflow rate selected by Carbon Engineering is 1.4 m/s [5].

\( d_{\text{tube}} \) does not enter Eq. 3 so \( d_{\text{tube}} = 50 \text{ \( \mu \)m} \) is a somewhat arbitrary choice. Applying Eq. 1 with \( d_{\text{tube}} = 50 \text{ \( \mu \)m} \) yields \( l_{\text{tube}} = 190 \text{ \( \mu \)m} \).

The pore dimensions (\( d_{\text{pore}} = 40 \text{ nm} \) and \( l_{\text{pore}} = 2 \text{ \( \mu \)m} \)) are discussed further in the Appendix. Here I provide two salient facts. (1) The capture site density on the pore surface is taken to be one per (4.3 Å)², approximately the capture site density reported for TiO₂(110) [13] and Fe₂O₄(001) [14]. With these pore specifications, \( d_{\text{tube}} = 50 \text{ \( \mu \)m} \), and \( v = 6 \text{ m/s} \), it takes 0.3 s for enough CO₂ to pass through the sorbent to fill the capture sites. (2) The characteristic time for diffusion into and out of the pores is \( \sim 0.03 \text{ s} \), so the capture rate is not limited by diffusion into the pores.

4. Energy consumption for dry air. In this section, the optimum adsorptive binding energy \( E_{\text{ad}} \) is calculated under an assumption that there is no H₂O in the atmosphere. A major factor in this calculation is the extrinsic energy cost to run the adsorption/desorption cycle: the energy that must be expended independently of the amount of CO₂ actually captured, for example in heating sorbent material other than the binding sites themselves. When the extrinsic energy consumption is low, energy efficiency is maximised when \( E_{\text{ad}} \) is relatively low, such that the occupation swing (the binding site occupation after the adsorption phase minus that after the desorption phase) is well below 100% [10]. When the extrinsic energy consumption is substantial, the occupation swing should be large.

The desorption pressure is set here to 2% of the ambient pressure: 1.3 kPa. This is, again, a value chosen for illustration, not a carefully-considered optimum. The occupation swing is calculated using the Langmuir model for adsorption: the density of binding sites is fixed, the rate of adsorption is proportional to the number of unoccupied sites, and binding is characterised by a single binding energy, \( E_{\text{ad}} \), that is independent of the number of adjacent sites that are occupied. Let \( n \) be the actual density of adsorbed CO₂ molecules on the pore surfaces. The probability that an incoming CO₂ molecule adsorbs is taken to be \( S \times (1 - n/n_{\text{sat}}) \), where \( S \) is the sticking fraction and \( n_{\text{sat}} = (4.3 \text{ Å})^{-2} \). \( S \) is set to 0.75, the value reported for gases impacting a TiO₂(110) surface at 32 K [17]. Let \( r_{\text{att}} \) be the attempt rate for desorption and \( r_{\text{in}} \) be the impact rate of CO₂ molecules on the sorbent surface. In equilibrium, the rate of escape equals the capture rate:
\[
r_{\text{att}} n \exp (-E_{\text{ad}}/k_B T) = \left(1 - \frac{n}{n_{\text{sat}}} \right) S r_{\text{in}}.
\]
For \( r_{\text{att}} \), a quantum-limited rate is taken as \( r_{\text{att}} = k_B T/h \), which evaluates to \( 2.8 \cdot 10^{13} \text{ s}^{-1} \) at 213 K. \( r_{\text{in}} \) is calculated from the pressure of the gas: \( P = \frac{3}{2} m_{\text{molec}} v_{\text{molec}} I \), where \( I \) is the impact rate and \( m \) is the mass of the dominant molecule. For the adsorption phase, rearranging this expression and taking into account the concentration of CO₂ and its slightly slower velocity yields:
\[
r_{\text{in}} = \frac{3}{2} \frac{4 \cdot 10^{-4}}{\sqrt{v_{\text{molec}} \mu}} \frac{65 \text{ kPa}}{V_{\text{molec}}(T)}.
\]
Taking \( m_{\text{air}} = 29 \text{ g/mol} \) and \( v_{\text{molec}} = (3k_B T/m_{\text{air}})^{1/2} = 430 \text{ m/s} \), \( r_{\text{in}} = 1.5 \cdot 10^{24} \text{ m}^{-2} \text{s}^{-1} \) at 213 K. For the desorption phase, the gas is taken to be pure CO₂:
\[
r_{\text{in}} = \frac{3}{2} \frac{1.3 \text{ kPa}}{2m_{\text{CO}_2} v_{\text{CO}_2}(T)}.
\]

The desorption temperature \( T_{\text{de}} \) is calculated as a function of \( E_{\text{ad}} \) and the adsorption temperature, \( T_{\text{ad}} \), which is equal to the ambient temperature. The energy required for desorption is taken to be \( E_{\text{ad}} \) for each molecule that is captured in the adsorption phase and released in the desorption phase, plus the energy required to heat the sorbent from \( T_{\text{ad}} \) to \( T_{\text{de}} \). I assume that there is no mechanism for recovering this heat. The sorbent is taken to have a heat capacity of 683 J/kg-K, which is the heat capacity of TiO₂ at room temperature [18]. Results are calculated for two sorbent capacities: 5 wt % CO₂ and 10 wt % CO₂. For silica aerogel functionalised with amine groups, capacities of up to \( \approx 10 \text{ wt %} \) have been demonstrated in atmospheres of 400 ppm CO₂ [19,21].

The criterion for \( T_{\text{de}} \) is that the captured CO₂ escapes the pores in \( \sim 0.3 \text{ s} \). Because the diffusion time out of the pores is \( \sim 0.03 \text{ s} \), this condition corresponds to a requirement that 10% of the adsorbed CO₂ molecules desorb instantly: if the pores were blocked so that no CO₂ could escape, 10% of the CO₂ molecules would desorb.
FIG. 2. (a) Desorption temperature range for $T_{\text{ad}}$ between $-90^\circ \text{C}$ and $-58^\circ \text{C}$, under a requirement that captured CO$_2$ molecules escape the pores in $\sim 0.3$ s. (b) The amount of CO$_2$ captured over the course of the year as a fraction of a hypothetical maximum in which the occupation swing is 100% and the capture machinery operates year-round. (c) Energy consumption for heating the sorbent per captured CO$_2$ molecule, and for two possible sorbent capacities. Results in panels (b) and (c) are averaged over the observed temperature distribution at the Vostok research station [11], with a cutoff temperature of $-58^\circ \text{C}$.

Results are shown in Fig. 2. Fig. 2(a) shows the range of desorption temperatures for $T_{\text{ad}}$ between $-90^\circ \text{C}$ and $-58^\circ \text{C}$, as a function of $E_{\text{ad}}$. Fig. 2(b) shows the amount of CO$_2$ captured as a fraction of a hypothetical maximum in which the occupation swing is 100% and the capture machinery operates year-round. For high $E_{\text{ad}}$, this fraction saturates at the fraction of the year the temperature is below $-58^\circ \text{C}$. Finally, Fig. 2(c) shows the average energy consumption per captured CO$_2$ molecule. The results in Figs. 2(b) and (c) are averaged over the temperature distribution at the Vostok station [11], with a $-58^\circ \text{C}$ cutoff.

Energy efficiency is maximised for $E_{\text{ad}}$ between 0.35 and 0.40 eV. For a sorbent capacity of 10 wt% CO$_2$, the energy consumption is about 1.0 eV per molecule, which can be divided into two parts: an intrinsic component, $\approx 0.4$ eV, to drive the desorption, and an extrinsic component, $\approx 0.6$ eV, to heat the rest of the sorbent. For comparison, the thermodynamic minimum possible energy expenditure to separate CO$_2$ at 213 K is 0.16 eV per molecule [16].

Also shown in Fig. 2 are results where the criterion for $T_{\text{de}}$ is maximum energy efficiency at each $T_{\text{ad}}$, without regard to the length of time required for desorption. Under this criterion, $T_{\text{de}}$ is lower and energy consumption is reduced by $0.1 – 0.2$ eV/CO$_2$.

$E_{\text{ad}} \approx 0.4$ eV has been observed experimentally for TiO$_2$ [14], Fe$_3$O$_4$ [15], and Cr$_2$O$_3$ [22]. The expansion in the range of materials that could be applied is a potentially important advantage of operation in Antarctica: a reduction in the optimum binding energy from $\approx 0.55$ eV at $25^\circ \text{C}$ to $\approx 0.40$ eV at $-60^\circ \text{C}$ constitutes, by itself, only a $\approx 30\%$ energy saving, but, in addition to these oxides, it opens up a range of zeolite and metal-organic framework materials for consideration [10]. It may also allow opportunities for adsorption modulated not by temperature but by, for example, electric charge [23, 24].

5. Purging H$_2$O. During the Antarctic winter, the relative humidity is generally around 100% [25]. The adsorption energy of H$_2$O to a TiO$_2$(110) surface is $\approx 0.9$ eV, as compared with $\approx 0.4$ eV for CO$_2$ [14]. Furthermore, except at cryogenic temperatures H$_2$O displaces adsorbed CO$_2$. If the sorbent material has similar binding energies for H$_2$O and CO$_2$ to TiO$_2$(111), a water front, a dividing line between sites occupied with H$_2$O and sites occupied with CO$_2$, is expected to develop in the pores. If the desorption phase is not energetic enough to desorb H$_2$O, this front will move deeper into the pores with each adsorption/desorption cycle, until there are no

FIG. 3. Optimum purge period as a function of $T_{\text{ad}}$. Every $N_{\text{purge}}$th desorption cycle is run at an elevated temperature to drive off H$_2$O, at an assumed energy cost of four times that for a regular desorption cycle.
sites available for capture of CO$_2$.

The idea explored in this section is to periodically purge adsorbed H$_2$O with a very hot desorption phase. Taking $E_{ad}$ for H$_2$O to be 0.9 eV, the desorption temperature is $\approx 800$ K, constituting a temperature swing about 3.5 times larger than during a regular desorption cycle. Let $N_{\text{purge}}$ be the purge period; every $N_{\text{purge}}$ th cycle runs hot, at an energy cost of four times that of a regular desorption cycle. Between purge cycles, the number of binding sites occupied with H$_2$O and unavailable for CO$_2$ capture increases linearly: after $n$ cycles, the fraction of binding sites occupied with H$_2$O is $n \times P_{\text{H}_2\text{O}} / P_{\text{CO}_2}$, where $P_{\text{H}_2\text{O}}$ is the vapour pressure of H$_2$O [26], and $P_{\text{CO}_2}$ that of CO$_2$. At an ambient pressure of 65 kPa, $P_{\text{CO}_2} = 26$ Pa.

$N_{\text{purge}}(T_{ad})$ calculated within this model is shown in Fig. 3. $N_{\text{purge}}$ at each $T_{ad}$ is chosen to minimise the energy cost of the purge cycles per captured CO$_2$ molecule. For simplicity, this calculation was performed assuming a 100% occupation swing on the sites available for CO$_2$ capture.

At $-58^\circ$ C, the H$_2$O purges add 85% to the energy consumption. Averaging over the temperature distribution below $-58^\circ$ C, the purges add 39% to the energy consumption for heating the sorbent per captured CO$_2$ molecule. This energy cost is included in Table II.

Reducing the binding energy of H$_2$O would improve energy efficiency, but in contrast to operation in temperate climates, it is not necessary that the binding energy for H$_2$O be less than that of CO$_2$. Ref. [10] identifies compounds where the physisorption binding energy of H$_2$O may be comparable to that of CO$_2$, making them good candidates for operation in Antarctica. A two-stage capture process may also be possible, in which the first stage captures most of the incoming H$_2$O at a lower binding energy, reducing the frequency of purge cycles in the CO$_2$ stage.

**6. The katabatic winds.** Katabatic winds are drainage winds. The surface of the high plateau cools through radiation to space [27]. Air in contact with the surface cools, compresses, and flows downhill. The katabatic winds are an obvious potential power source because they are exceptionally strong and constant, and are strongest in winter, when the capture machinery operates. They are strongest around the perimeter of the ice sheet, so power would need to be transmitted to the high plateau where the capture machinery is sited. The katabatic winds hug the surface: the wind velocity is highest 100-200 m above the surface [28], matching the typical hub height of modern wind turbines.

How many turbines are required? The average winter wind speed 100 m above ground level exceeds 20 m/s over $1.5 \times 10^6$ km$^2$ of Antarctica [28]; turbines can be placed in these areas. Suppose an energy consumption of 2 eV per captured CO$_2$ molecule and operation for six months of the year. To capture 10 Gt CO$_2$/y, the power consumption is 3 TW during these six months. Set the rotor diameter to 100 m, and the mean turbine separation to 2 km; at this ratio of separation to rotor diameter the power generated by each turbine is $\approx 85\%$ of that generated by isolated turbines [29]. The air density to 1.3 kg/m$^3$, corresponding to an elevation of 1000 m and a temperature of $-25^\circ$ C. With these parameters, each turbine generates $\approx 20$ MW, and $\approx 1.5 \times 10^5$ turbines distributed over $\approx 5 \times 10^8$ km$^2$ are required. The power generated per unit land area is $\approx 6$ W/m$^2$.

I conclude this section by noting that erection of an immense number of turbines around the perimeter of the east Antarctic ice sheet may offer a climactic benefit: if they slow the meridional circulation over the ice sheet, the high plateau might cool further, allowing even more efficient capture and storage of CO$_2$.

**7. Storage.** Two possible storage schemes for the captured CO$_2$ are illustrated in Fig. 4. Panel (a) illustrates a scheme in which CO$_2$ is injected into the ice. Machines, labelled A in the figure, might guide the opening of the space for the CO$_2$, determining its depth below the surface. If it is $\approx 1$ km beneath the surface, then the ice sheet above will be lifted by CO$_2$ injected at a pressure of 10 MPa. 1000 m beneath the surface, the ice temperature is $\approx -47^\circ$ C [32, 33]; at 10 MPa and $-47^\circ$ C, CO$_2$ is
a liquid. To reduce the risk of seepage, after injection the CO₂ could be solidified by circulating a working fluid to the surface when the surface temperature is well below the triple point of CO₂, −57°C. The CO₂ could also be injected as a slurry with water ice. 10 Gt/y of CO₂ corresponds to 6.3 km³/y; if the CO₂ seam has an area of 10⁴ km², the ice sheet gets lifted by 60 cm/y.

The energy required to compress CO₂ from 1.3 kPa to its triple point pressure, 515 kPa, is ≈ k₝T log(515 kPa/1.3 kPa) ≈ 0.1 eV/molecule. Under an assumption of 50% efficiency, 0.2 eV per molecule is allocated for compression in Table II. Above 515 kPa, CO₂ is liquid, so the energy cost for further compression to 10 MPa is taken to be negligible. The energy required to compress CO₂ from 10 MPa is well under 0.1 eV per molecule.

In Fig. 4(b) illustrates a second possibility: storage of captured CO₂ as snow on the surface. CO₂ snow gets injected between insulating layers, and the upper layer rises as the CO₂ accumulates. Storage of CO₂ as snow on the Antarctic surface was proposed in Ref. [34]. If the density of the CO₂ snow is, like water snow at a depth of more than a few metres [30], around half the density of void-free solid CO₂, then to store 10 Gt/y at a layer thickness of 50 m, as indicated in the figure, requires 250 km³/y. The vapour pressure of CO₂ reaches 65 kPa at −83.8°C [31], 28 K below the annual mean temperature at the Vostok station [11]. Thermal insulation for buildings has a typical thermal conductivity of 0.04 W/m-K [35]. If the insulating layers are 2 m thick and have this thermal conductivity, the average heat flux is 1.1 W/m², or 280 MW for a year’s worth of CO₂. The insulating layers could be provided with refrigeration to counter this heat flow: it is a vastly smaller amount of energy than that required to capture the CO₂ in the first place. Should the refrigeration fail, the CO₂ layer would take about 700 years to sublime.

8. Conclusion. Physisorption is widely regarded as impractical for direct air capture of CO₂ in temperate climates, due to the quantity of H₂O in the atmosphere. It may, however, be practical during the Antarctic winter. The much lower concentration of H₂O in the atmosphere and the lower binding energies required may open new routes for economical DAC on a gigatonne per year scale.

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APPENDIX

Here the pore dimensions are discussed further. The rate at which CO₂ is delivered to the inner lining of the sorbent tubes is given by:

\[ R_{\text{CO}_2} \approx \frac{v \times \pi (d_{\text{tube}}/2)^2 n_{\text{CO}_2}}{\pi d_{\text{tube}} l_{\text{tube}}} = \frac{v d_{\text{tube}} n_{\text{CO}_2}}{4 l_{\text{tube}}}. \]

\( n_{\text{CO}_2} \) is the numerical concentration of CO₂ in the incoming air, which, at an air density of 1.1 kg/m³, is 9.1·10²¹ m⁻³. \( R_{\text{CO}_2} \) evaluates to 3.6·10²¹ m⁻³ s⁻¹.

At short times, CO₂ diffuses into the pores faster than it can be delivered by the flow, and so the amount of CO₂ captured increases linearly in time. Supposing, for a moment, that the pores were infinitely long, there would eventually be a crossover to a diffusion-limited regime where the amount of CO₂ captured increases as \( \sqrt{t} \). Let \( t_0 \) be the crossover time, and \( l_0 \) the depth that the CO₂ penetrates at time \( t_0 \). \( l_0 \) can be obtained from a condition that the flux due to diffusion, which is the diffusion constant \( D_{\text{pore}} \) multiplied by the concentration gradient, matches \( R_{\text{CO}_2} \):

\[ R_{\text{CO}_2} = D_{\text{pore}} \frac{n_{\text{CO}_2}}{l_0}. \quad (7) \]

In Fig. 1, \( d_{\text{pore}} = 40 \text{ nm} \) is indicated, which is less than the mean free path in air (65 nm at 293 K and 101 kPa [36]). Therefore it is reasonable to estimate \( D_{\text{pore}} \) in the molecular limit: \( D_{\text{pore}} \approx d_{\text{pore}} v_z \), where \( v_z \) is the thermal velocity along the axis of the pore. \( \frac{1}{2} m_{\text{CO}_2} v_z^2 = \frac{1}{2} k_B T \), where \( m_{\text{CO}_2} \) is the mass of a CO₂ molecule, yielding \( v_z = 200 \text{ m/s} \) at \( T = 213 \text{ K} \).

In the mass-transport-limited regime, the front of sites occupied with CO₂ moves inward at rate \( R_{\text{CO}_2}/n_{\text{sat,3D}} \), where \( n_{\text{sat,3D}} \) is the adsorption site density in m⁻³. \( n_{\text{sat,3D}} \) is given by:

\[ n_{\text{sat,3D}} \approx n_{\text{sat}} \times \pi d_{\text{pore}} \times \frac{4}{\pi d_{\text{pore}}^2} \equiv \frac{\beta}{d_{\text{pore}}}. \]

Here, a constant \( \beta \) has been introduced, that, for \( n_{\text{sat}} = (4.3 \text{ Å})^{-2} \), evaluates to \( \beta = 2.2 \cdot 10^{19} \text{ m}^{-2} \). Taking \( t_0 \) from Eq. 7 and dividing by the velocity of the occupation front yields an expression for \( t_0 \):

\[ t_0 = \frac{v_z n_{\text{CO}_2} \beta}{R_{\text{CO}_2}^2}. \quad (8) \]

\( t_0 \) evaluates to \( \approx 3 \text{ s} \), independent of the pore diameter. For \( d_{\text{pore}} = 40 \text{ nm} \), \( l_0 \approx 20 \mu\text{m} \). \( l_{\text{pore}} \) is chosen to be a tenth of this to ensure rapid diffusion of CO₂ out of the pores during the desorption cycle.

* C.Hicks.1 (at) bham.ac.uk

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