The potential of direct air capture using adsorbents in cold climates

Highlights

DAC using adsorbents in cold climates has breakthrough synergistic effects

Readily available industrial zeolites are the most promising materials for DAC

Lowest reported energy penalty to capture and concentrate CO₂ from air

Deployment in cold climates can be a solution to global warming
Global warming threatens the entire planet, and solutions such as direct air capture (DAC) can be used to meet net-zero goals and go beyond. This study investigates using DAC in a 5-step temperature vacuum swing adsorption (TVSA) cycle with adsorbents’ Li-X and Na-X, readily available industrial zeolites, to capture and concentrate CO2 from air in cold climates. From this study, we report that Na-X in cold conditions has the highest known CO2 adsorption capacity in air of 2.54 mmol/g. This combined with Na-X’s low CO2 heat of adsorption, and fast uptake-rate in comparison to other benchmark materials, allowed for Na-X operating in cold conditions to have the lowest reported DAC operating energy of 1.1 MWh/tonCO2. These findings from this study show the promise of this process in cold climates of Canada, Alaska, Greenland, and Antarctica to be part of the solution to global warming.

INTRODUCTION

Global warming is being driven by increasing levels of CO2 in the atmosphere which increases global surface temperatures. The effects of global warming are particularly worrisome for polar ice-capped regions, like Greenland and Antarctica; these regions experience more significant warming than the rest of the planet and as sea levels rise, many coastal populations will have to be displaced. To mitigate the consequences of global warming, researchers, companies, and governments are investing time and effort into finding ways to effectively reduce the amount of CO2 entering the atmosphere or to capture CO2 directly from the air. The latter, direct air capture (DAC), is a technology that captures CO2 directly from the air and concentrates it. When coupled with geological storage, DAC can be used to sequester the CO2 permanently into the earth as a means of restoring earth’s CO2 atmospheric concentrations.

One of the main technological challenges for DAC is that CO2 in air is dilute, and capturing 1 ton of CO2 would require approximately 1,400,000 m3 of air. Because the concentration of CO2 in air is so low, it is uneconomical to significantly change the input air conditions (e.g., temperature, pressure, and humidity) during the capture step of a DAC process. Thus, the climate where a DAC plant operates is an important consideration for the economic feasibility of the process. Across the globe, mean annual temperatures vary from −41 to 36°C and mean annual humidity varies from 0.12 gH2O/kgair to 22 gH2O/kgair. Therefore, choosing a location where the climatic temperature and humidity are beneficial to the DAC process can improve the technology’s efficiency and reduce its operating costs.

The ideal temperature and humidity conditions for a DAC process varies based on the nature of the technology. Promising DAC technologies include chemisorption based processes such as amine based sorbents, absorption using caustic solutions, and CaO weathering, as well as physisorption based processes using zeolites and metal organic frameworks (MOFs). To date, little work has been done to identify favorable climates and locations for the aforementioned DAC technologies. In general, technologies using absorption of caustic solutions favor climates with high relative humidity to minimize water losses. Furthermore temperatures should always remain above 0°C to prevent damage similar to water cooling towers. On the other hand, technologies such as amine based sorbents require moist air to prevent degradation of the amines and higher temperatures to maintain acceptable CO2 uptake rates.

Relative to chemisorption, physisorption technologies require less sorbent regeneration energy because the CO2 capture is governed by relatively weaker van der Waals forces. However, adsorbents such as zeolites and MOFs typically require the water to be removed before the separation of the CO2.
them favor dry climates. Drier climates are primarily located closer to the poles which are on average much colder. Coincidentally, physisorption DAC technologies benefit from cold climates.

DAC technologies employing zeolites and MOFs have synergistic effects with cold climates which increases their economic viability as a part of the solution to global warming. First, separations are more thermodynamically favorable in colder climates (assuming the same feed stream composition). The equation in Figure 1, derived from the second law of thermodynamics, demonstrates that the temperature impacts the minimum work ($W_{\text{min}}$) required to separate and concentrate CO$_2$ (Equation 3 in the STAR Methods). As the temperature decreases, $W_{\text{min}}$ decreases substantially. For example, the energy requirements are 45% lower at $-50^\circ$C relative to $50^\circ$C.

The second synergistic effect is that adsorbents can adsorb significantly more CO$_2$ at colder temperatures; due to the exothermic nature of adsorption, zeolites and MOFs have higher adsorption capacities at lower temperatures. To illustrate the relationship between temperature and adsorption capacity, the Van’t Hoff equation (Equation 1) can be used. As temperature ($T$) decreases, the Henry’s Law constant ($K$) increases exponentially. The exponential increase in Henry’s Law constant is analogous to the exponential increase in adsorption capacity ($q_e$) for low concentrations of CO$_2$ (Equation 2). The benefits of the increase in adsorption capacity at low temperatures is twofold; firstly, the capital cost of the process decreases with the system being able to be designed with less adsorbent per ton of CO$_2$ captured; and secondly, the operating cost of the system decreases with less adsorbent required to be heated and evacuated per cycle per ton of CO$_2$ capture, reducing mechanical and thermal energy requirements.
\[ \ln K = -\frac{\Delta H_{\text{ads}}}{R} \frac{1}{T} + \ln K_0 \]  
(Equation 1)

\[ K = \frac{q_v}{C} \]  
(Equation 2)

With cold climates being 1) thermodynamically more favorable for separations; 2) adsorbents (physisorbents) adsorbing significantly more CO₂ in colder conditions; and 3) there being a miniscule amount of water in cold climates to separate prior to separating the CO₂, would locating an adsorbent-based DAC process in the coldest and driest regions of the planet be an instrument in solving global warming? In this study, we investigate the possibility of using affordable and industrially available zeolites, Na-X and Li-X, in a DAC process located in cold locations such as Canada, Alaska, Greenland, and Antarctica, as a means to reach net-zero and go beyond. This study will demonstrate DAC using a 5-step temperature vacuum swing adsorption (TVSA) cycle on an outdoor experimental unit between 58°C and −58°C. A common methodology in literature\(^8\)\(^{,34,36}\) will be used to calculate the energy requirements for DAC to compare results with that of other existing DAC technologies.

**Process**

To repeatedly utilize adsorbents to capture and concentrate CO₂, the conditions that are applied to the adsorbent are cycled. In literature, this has typically been done by cycling the temperature,\(^28\)\(^{,29,37}\) or temperature & vacuum to repeatedly capture and concentrate the CO₂ from the air. The latter method, known as TVSA, is used in this study due to the ability to significantly increase the purity to 95% which is required for pipelining the CO₂. Figure 2 illustrates the 5-step TVSA process\(^36\) used in this study. Note that the adsorption column was packed with Na-X or Li-X zeolites (inexpensive and commercially available zeolites).

The TVSA cycle begins with the adsorption step: atmospheric air is blown through a desiccant bed to remove any moisture and is then directed to the adsorption column packed with the Na-X or Li-X zeolite. The column captures CO₂ as well as some N₂, O₂, and Ar from the air at ambient temperature (\(T_A\)) and pressure (\(P_A\)). Once the adsorbent is saturated with CO₂, the blowdown step begins: the adsorption column is isolated by shutting valves, and a vacuum is applied to the column (\(P_B\)). Note that this vacuum is enough to remove weakly adsorbed components from the column (e.g., N₂, O₂, and Ar) while retaining the more strongly adsorbed CO₂. After blowdown, the evacuation step begins: the adsorption column is heated to 200°C (\(T_E\)) by means of a heater and a stronger vacuum (\(P_E\)) is applied, thereby releasing the CO₂ from the adsorbent. The CO₂ stream exiting the vacuum pump (i.e., the high purity CO₂) is the product of the TVSA cycle. The adsorption column is then brought back to atmospheric pressure in the pressurization step by feeding in dry air from the exit of the adsorption step. The desiccant bed (used to dry the air prior to the adsorption step) is then regenerated in the waterbed regeneration step: dry air from the adsorption column is passed through the adsorption column to pick up any sensible heat to produce hot dry air. This hot dry air is then used to regenerate the desiccant. If further heating is required to regenerate the desiccant, additional heat can be applied using a heater. The 5-step TVSA process is then repeated. This TVSA cycle was used to determine the energy required for the process.

**RESULTS AND DISCUSSION**

To determine the energy required to capture one ton of CO₂ using the 5-step TVSA cycle, a similar methodology to many sources in literature\(^8\)\(^{,34,36}\) was used (see section S.1.5 for detailed calculations). To calculate the energy requirements, the heat of adsorption of CO₂ on the zeolite should be known because it impacts the desorption energy required for the sorbent regeneration. To obtain the heat of adsorption, the pure component adsorption isotherms of CO₂ were measured at 10°C, 30°C, 50°C, 70°C, and 90°C for both the Li-X and Na-X zeolites, which provides their adsorption capacities (Figures S3 and S4 display isotherms). Then, the Clausius-Clapeyron equation was applied to determine the isosteric heat of adsorption as a function of adsorption capacity (Figure 3). With increasing adsorption capacity, the heat of adsorption for both zeolites decreases slightly. This is an indication of the zeolites’ heterogeneous nature and indicates that the higher energy sites will be adsorbed first before the lower energy ones are filled. The heat of adsorption of CO₂ on Li-X varies from 54 kJ/mol to 49 kJ/mol, which is higher than that of Na-X, which varies from 49 kJ/mol to 44 kJ/mol. These results are in accordance with values reported in the literature where the heat of adsorption at 395 ppm of CO₂ for Li-X and Na-X were...
51 kJ/mol and 45 kJ/mol, respectively. \(^\text{10}\) Because Li-X adsorbs CO\(_2\) more strongly than Na-X, more thermal energy is required to regenerate Li-X relative to Na-X.

To investigate the energy requirements for the 5-step TVSA cycle, breakthrough experiments were performed on a 1.09 cm diameter, 14.5 cm long fixed column packed with 9.5g of Li-X and Na-X pellets. Seven experiments were conducted between 58°C and −58°C to reveal the nature of the adsorption step, including the adsorption capacities and capture fractions of the zeolites. Atmospheric air from Ottawa (Canada) was conditioned using a temperature-controlled bath to simulate a wide variety of ambient temperatures found on Earth. The conditioned air was first dehumidified by flowing it over a desiccant bed, and then fed into the adsorption column at 2500 sccm. The exiting CO\(_2\) gas concentration from the adsorption column during the adsorption step for Li-X and Na-X were measured over time (Figure 4).

At the beginning of the breakthrough, the adsorbent near the inlet adsorbs the CO\(_2\) from the air. This measures an outlet concentration of CO\(_2\) of 0 ppm. With time, when the initial adsorbent becomes saturated and the mass transfer zone approaches the outlet, the CO\(_2\) concentration begins to increase. After a certain time, the adsorbent in the column becomes fully saturated (i.e., can no longer retain any CO\(_2\)) and thus, the
outlet CO2 concentration is the same as the inlet. From Figure 4, we see that the CO2 breakthrough time increases as the temperature cools. This indicates that the adsorption capacity increases with cooling temperature. Using these breakthrough curves, the zeolite’s adsorption capacity at each temperature can be calculated by integrating the area between the input and output concentrations. To account for slight variations in inlet CO2 concentrations, the Henry’s Law relationship (Equation 2) was applied to normalize the adsorption capacities to 420 ppm. The normalized CO2 adsorbent capacity of Li-X and Na-X, as a function of temperature, with their uncertainties are reported in Figure 5. The results from Figure 4 align closely with DAC breakthroughs in literature at 20 and 25°C from similar types of faujasite type zeolites.10,36,38

As expected, the zeolites’ adsorption capacity increases with colder temperatures (Figure 5). The exact adsorption capacities for Li-X are 0.31, 0.47, 0.77, 1.3, and 1.9 mmol/g at temperatures of 20°C, 1°C, –20°C, –40°C, and –58°C, respectively. For Na-X, the adsorption capacities are higher, at 0.30, 0.65, 1.1, 1.9, and 2.5 mmol/g at 20°C, 0°C, –20°C, –40°C, and –58°C, respectively. Note that an adsorption capacity of 2.5 mmol/g from ambient air concentrations (i.e., 420 ppm) surpasses the highest known CO2 adsorption capacity reported to date, which are 2.1 mmol/g, for NbOFFIVE-1-Ni (–15°C).35

The adsorption step temperature ($T_a$, Figure 2) likewise influences, in two ways, the adsorption capture fraction (defined in the STAR Methods in Equation 7). First, as the temperature cools, the breakthrough time is extended, which increases the capture fraction. However, colder temperatures can decrease the rate of Knudsen diffusion and molecular diffusion in the zeolite, which increases the duration of the mass transfer zone, thereby decreasing the capture fraction. Thus, the effects of temperature on the capture fraction can have varying effects depending on the adsorbent. For example, when the adsorption step is stopped when the exiting CO2 concentration reaches 95% of the input concentration, the capture fraction for Li-X remains around 91.5 ± 0.5% whether the temperature is 58°C or –58°C. In other words, Li-X’s capture fraction does not improve at lower temperatures because the two aforementioned effects of temperature on the capture fraction are opposing. However, with Na-X zeolite, the capture fraction improves from 71.6% (at 58°C) to 91.5% when the temperature is decreased to –58°C.

![Figure 3. CO2 isosteric heat of adsorption values using the Clausius-Clapeyron equation for Li-X and Na-X](image-url)
Figure 4. Breakthrough curves of CO$_2$ during the adsorption step with varied temperatures from 58°C to –58°C for Li-X (top) and Na-X (bottom).
The increase in adsorption capacity with colder temperatures improves the economics of the 5-step TVSA process because it lowers overall energy requirements; with the most prominent energy savings from the evacuation step. During the evacuation step, a certain amount of thermal energy ($E_3$) is required (per ton CO$_2$ captured) to heat the adsorbent to the desorption temperature. As the adsorption capacity increases, the ratio between the sensible energy required to heat the adsorbent over the amount of CO$_2$ captured decreases (detailed calculations can be found in S.1.5). For example, when lowering the temperature from 20°C to −58°C, $E_3$ decreases from 3.1 to 0.73 MWh/tonCO$_2$ for Li-X, and 3.1 to 0.56 MWh/tonCO$_2$ for Na-X (Figure 6).

The higher adsorption capacity at colder temperatures during the adsorption step also reduces the vacuum energy ($E_V$) required during the blowdown step for Li-X and Na-X, and the energy for flow from the adsorption step ($E_F$) for Na-X. Although $E_V$ decreases, the resulting energy savings are negligible compared to the vacuum energy required to remove the CO$_2$ during the evacuation step. However, the energy savings for flow from the adsorption step are more significant; at −58°C, $E_F$ is 10% lower than at 20°C Na-X (Figure 6).

Colder temperatures also increase the temperature difference between the adsorption step and the evacuation step ($\Delta T$) which affects both $E_2$ and $E_D$ (CO$_2$ desorption energy, sensible + latent). For $E_2$, the increase in $\Delta T$ is a lesser effect than the increase in adsorption capacity, leading to an overall decreased energy requirement. For $E_D$, the larger $\Delta T$ increases the sensible energy required to heat up the adsorbed CO$_2$ to the evacuation temperature. Because of the lower desorption energy at warmer temperature, both zeolites require 5% more energy at −58°C than 20°C.

The concentration of CO$_2$ in the air around the globe is relatively constant at 0.64 g$_{CO2}$/kg$_{air}$ (420 ppm) whereas the mean annual humidity varies from 0.12 g$_{H2O}$/kg$_{air}$ in Antarctica to 22 g$_{H2O}$/kg$_{air}$ in the Amazon. For this 5-step TVSA cycle, water is removed from the air prior to capturing CO$_2$. Thus, the geographical location of this process is an important consideration because it will affect the humidity of the incoming air.

Figure 5. Adsorption step temperature effect on CO$_2$ adsorption capacity at 420 ppm for Li-X and Na-X with their associated uncertainties.
Figure 6. Effect of adsorption step temperature on the energy requirements per ton of captured CO₂ for Li-X (top) and Na-X (bottom)
air, and therefore energy required to desiccate the air. The heat energy required to regenerate the wa-

terbed ($E_W$) for Na-X as a function of temperature (20 to $-58^\circ C$) and humidity (25%–100% RH)\textsuperscript{39} was calcu-

lated using the heat of adsorption from the desiccant (silica gel),\textsuperscript{40} and the previously calculated parame-

ters from the breakthrough experiments (Figure 7). For $-19^\circ C$, $-37^\circ C$, and $-58^\circ C$, the sensible energy in

the zeolite bed is sufficient to regenerate the desiccant. However, at 0 and 20$^\circ C$, additional energy is

required to regenerate the desiccant bed with $E_W$ accounting for the majority of the energy requirement

for the process at higher humidities and temperatures. This is because there is more water in the air at

warmer temperatures than colder temperatures. Because desiccation is a crucial step in the 5-step TVSA

process, it is evidently more economical to operate in a low humidity location.

To determine a material’s potential for DAC, other than comparing energy requirements of the process, the

CO$_2$ uptake rate (or rate constant), heat of sorption, and adsorption capacity (at 420 ppm) have been used as

benchmark parameters.\textsuperscript{34,35} A faster CO$_2$ uptake rate is favored because it improves the capture fraction of

CO$_2$ (thereby reducing operating cost), and it facilitates the design of higher space velocities through the sys-

tem, which reduces capital costs. For amines such as MEA and DEA, CO$_2$ uptake rates are roughly an order of

magnitude slower than caustic solutions of NaOH.\textsuperscript{34} For that reason, the American Physical Society (APS) cate-

gorized amines as unideal for DAC.\textsuperscript{34} Adsorbents such as zeolites, however, have very fast uptake rates; their

porous nature enables gas to diffuse directly to adsorption sites primarily via molecular and Knudsen diffusion.

For example, the uptake rates for Li-LSX, Na-X, and K-LSX are $2.2 \times 10^{-2}$ s$^{-1}$, $2.4 \times 10^{-2}$ s$^{-1}$, and $1.6 \times 10^{-2}$ s$^{-1}$, respectively at 25$^\circ C$.\textsuperscript{10} The uptake rates of these zeolites are two orders of magnitude faster than that of amines such as amine-grafted SBA-15 whose uptake rate is $4.3 \times 10^{-4}$ s$^{-1}$ when dry and $1.4 \times 10^{-4}$ s$^{-1}$ when wet.\textsuperscript{10} For this study, the fast uptake rates are shown from the steep slope of the breakthrough curves (Figure 4)

even at interstitial air velocities of 1.1 m/s ($0^\circ C$) through the bed.

In addition, zeolites have high adsorption capacities at cold temperatures and low heats of adsorption

when compared to other key benchmark and novel materials (Figure 8).\textsuperscript{28,29,24,35,41,42} As discussed, lower

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure7.png}
\caption{Total energy requirements of the process between 0 and $-58^\circ C$ including the additional energy required to regenerate waterbed for relative humidity between 25 and 100%}
\end{figure}
CO₂ heats of sorption reduce the energy required to regenerate the sorbent, and higher sorption capacities reduce operating and capital costs. Although Na-X and Li-X have low heats of sorption, they become more promising materials for DAC application at colder temperatures due to their increased adsorption capacities. This is shown with the adsorption capacity increasing at colder temperatures and surpassing many novel DAC materials like MOF SIFSIX-3-Cu as well as benchmark materials like amine TRI-PE-MCM-41 (Figure 8). Thus, at cold temperatures, the combination of Na-X’s fast uptake rate, low heat of adsorption, and largest adsorption capacity (at 420 ppm CO₂) makes it the most promising adsorbent for DAC (which agrees with calculations for energy requirements). Other benchmark materials like MOFs also perform better in cold temperature with reported values for Nb-OFFIVE-1-Ni increasing from 0.94 mmol/g at 35°C to 2.1 mmol/g at −15°C.

To exploit Na-X’s potential for CO₂ capture, the DAC process must operate in a cold climate such as Antarctica which ranges from −2.3°C to −41.1°C, with an average annual temperature of −31.4°C. Figure 9 compares the 5-step TVSA process using Na-X from this work in cold conditions to other existing DAC technologies. Looking at energy requirements, our process was compared with: 1) APS’s NaOH based process, 2) Carbon Engineering’s KOH based process, 3) Climeworks’ amine grafted NFC, Sabatino et al. APDES-NFC, and Sabatino et al. Lewatit VP OC 106, whose energies were all calculated for warm conditions. These comparisons were selected because they consider real-world conditions for where a DAC using such a technology would be located such as humidity that is present within the air which impacts the energy requirement significantly for amine solid sorbent based processes. For DAC technologies of Na-X, NaOH, and KOH, the final product that is produced is 15 MPa dry CO₂, which is ready to be pipelined. For APDES-NFC, and Lewatit VP OC 106 the final product is a 15Mpa wet CO₂ which would require desiccation before pipelining. For Climeworks’ amine grafted NFC, the energies reported are from their Hellisheiði plant which produces a lower pressure wet CO₂ which is mixed with water, pumped, and sequestered underground in Iceland.

Out of the six materials compared in Figure 9, the cold temperature for the 5-step TVSA cycle using Na-X exhibits the lowest known reported energy requirements for DAC of CO₂ of 1.23 MWh/tonCO₂. With
energy making up the majority of the cost of DAC,\textsuperscript{44} this low energy cost makes DAC in cold climates using Na-X an economically accessible solution for reducing atmospheric CO$_2$ concentrations, with the potential of reversing the effects of global warming.

Capital cost is an important consideration for a technology’s viability. Benchmarked materials, such as amines grafted or impregnated onto porous substrates, are not commercially available and have short sorbent lifetimes due to oxygen degradation\textsuperscript{32} which makes their capital costs relatively high. However, Na-X is an industrially available zeolite with a working lifetime over 15 years in similar separations such as air purification units before air separation units.\textsuperscript{45} This long lifetime makes its potential use in DAC processes even more interesting.

Implementing this DAC technology as a tool to solving global warming requires the future DAC plant to be in a favorable climate, placed next to a clean abundant renewable inexpensive energy source to power the DAC plant, in addition to being located next to a nearby CO$_2$ sequestration site to store the CO$_2$ permanently. By placing a DAC plant with all three of these characteristics, the plant in the favorable climate will avoid costly electricity transmission infrastructure and expensive CO$_2$ pipelines. One promising energy source for cold weather DAC technology includes winds which are the strongest nearer the poles such
as Antarctica’s or Greenland’s high quality katabatic winds. These katabatic winds are dense, persistent, with wind velocities above 10 m/s, that have relatively consistent wind direction, and are considered the world’s strongest winds. Taking advantage of these strong winds in the large scale, can provide the needed energy economically for the implementation of a gigaton DAC plant. To determine the potential for CO2 sequestration, normally in-depth geology of the locations is used. However, due to the remoteness of these polar regions, little geologic surveying has been done with the exception of the US Geological Survey oil and gas potential and the vast sedimentary basins surrounding the coastlines of Canada, Alaska, Antarctica and Greenland which both highlights the strong potential for deep underground CO2 sequestration.

Although the implementation of gigaton Na-X DAC plants in cold climates such as Canada, Alaska, Greenland, and Antarctica could be challenging from a physical standpoint (e.g., lack of infrastructure and personnel), the benefits are unquestionable. These locations have the ideal climate for this 5-step TVSA process, high renewable energy prospects, and have the potential for on-site CO2 sequestration. Unlike existing DAC technologies that operate in moderate climates, the implementation of a gigaton DAC plant using this 5-step TVSA process would have minimal impact on human and animal life because it would be located in a remote location and occupy uninhabitable lands. If the physical challenges of operation in these barren cold locations like Greenland and Antarctica are overcome, DAC using adsorption in cold climates can be an economical tool to reach net-zero and go beyond by reducing CO2 levels in the atmosphere efficiently, contributing to reversing global warming.

Conclusion
The use of inexpensive and commercially available zeolites for the DAC of CO2 was explored. Na-X and Li-X were studied in a 5-step TVSA process over a wide range of atmospheric conditions (i.e., temperature and humidity) and we demonstrated how cold temperature operation could be the key to an economically feasible DAC process. Because of the synergistic effects between the adsorbent and the process when operating at cold temperatures, energy requirements as low as 1.1 MWh/tonCO2 to capture and concentrate CO2 were reported for the first time.

This work shows the potential of these adsorbents which have low CO2 heats of adsorption, fast uptake-rates, and in cold conditions high CO2 adsorption capacities in comparison to other benchmark and novel materials. For adsorbents in cold conditions, Na-X had the highest known adsorption capacity for CO2 at atmospheric concentrations and, we showed how the total energy requirements can be as low as 1.13 MWh/tonCO2 which is 39–72% lower than benchmark the DAC technology. These significant energy savings are possible due to three synergistic mechanisms between cold temperatures and the 5-step TVSA process: separations are thermodynamically more favored in cold climates (Second Law of Thermodynamics), adsorbents perform DAC separations better in colder conditions, and less water is present in the air, thereby reducing the water penalty in colder environments. Thus, the frigid Canadian, Alaskan, Antarctic or Greenlandic climate combined with plentiful winds and sequestration potential can provide the optimal location for large scale inexpensive DAC installation which has the potential of removing CO2 from the atmosphere as a way to reverse global warming. Further work is underway to use the learning gained from Na-X and Li-X to explore other existing materials that have potential to be used for DAC of CO2 in cold climates.

Limitations of the study
Implementation of DAC plants in cold climates is a challenge that requires rigorous planning and cold weather engineering to deal with the lack of infrastructure and frigid temperatures in these cold remote locations. From an engineering perspective, frigid temperatures impact lubricant, material, static protection, and elastomer choices which therefore requires unique solutions for many technology implementations. Frigid temperatures are also hostile to humans, and when combined with the remoteness of these locations, can be deadly without proper planning. This remoteness brings a lack of basic infrastructure such as communication, medical, transportation, and social infrastructure, let alone mental challenges for humans. Many of these challenges have been noted and overcome in deployments in Northern Canada, Svalbard, Alaska, Greenland, Russia, and Antarctica in mining, oil, & gas industries as well as in research and habitation. An example of this ability to overcome cold conditions, Antarctica, the coldest climate on Earth, has roughly 30 countries with 82 bases set-up supporting 5000 personnel with advanced research...
equipment such as the South Pole Telescope, IceCube Neutrino Observatory, and Askaryan Radio Array. Similarly for deployment of DAC plants in cold climates, rigorous planning and preparation is needed overcome these cold climate challenges.

NOMENCLATURE

\[ C = \text{Concentration (atm}^{-1}\text{)} \]
\[ E_C = \text{Energy Required for Compression (MWh tonCO}_2^{-1}\text{)} \]
\[ E_D = \text{Energy Required for Desorption (MWh tonCO}_2^{-1}\text{)} \]
\[ E_F = \text{Energy Required for Flow (MWh tonCO}_2^{-1}\text{)} \]
\[ E_S = \text{Energy Required for Sorbent (MWh tonCO}_2^{-1}\text{)} \]
\[ E_T = \text{Total Energy Required for the Process (MWh tonCO}_2^{-1}\text{)} \]
\[ E_V = \text{Energy Required for Vacuum (MWh tonCO}_2^{-1}\text{)} \]
\[ E_W = \text{Additional Energy Required for Waterbed Regeneration (MWh tonCO}_2^{-1}\text{)} \]
\[ K = \text{Henry’s Law Constant (mmol g}^{-1}\text{ K}^{-1}\text{)} \]
\[ H_A = \text{Heat of Adsorption (kJ mol}^{-1}\text{)} \]
\[ H_0 = \text{Heat of Adsorption at Zero Loading (kJ mol}^{-1}\text{)} \]
\[ M_{CO}_2 = \text{Molar Mass of CO}_2 (\text{g mol}^{-1}\text{)} \]
\[ P = \text{Pressure (atm)} \]
\[ q_e = \text{Adsorption Capacity (mmol g}^{-1}\text{)} \]
\[ R = \text{Gas Law Constant (J mol}^{-1}\text{ K}^{-1}\text{)} \]
\[ T = \text{Temperature (K)} \]
\[ y = \text{Mole Fraction} \]
\[ W_{min} = \text{Minimum Work to Concentrate Gas to 100% (MJ tonCO}_2^{-1}\text{)} \]

STAR METHODS
Detailed methods are provided in the online version of this paper and include the following:

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SUPPLEMENTAL INFORMATION
Supplemental information can be found online at https://doi.org/10.1016/j.isci.2022.105564.

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AUTHOR CONTRIBUTIONS
S.W. conceived and performed experiments, analyzed results, and wrote the manuscript.

DECLARATION OF INTERESTS
Sean MW Wilson is a shareholder of TerraFixing Inc.
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STAR★METHODS

KEY RESOURCES TABLE

| REAGENT or RESOURCE | SOURCE | IDENTIFIER |
|---------------------|--------|------------|
| Chemicals, peptides, and recombinant proteins | CO₂ (99.99%) | CAT# 24001324 |
| Other (Adsorbents) | Li-X | CECA Arkema Group CAT# Siliporite_Nitroxy_SXSDM |
| | Na-X | CECA Arkema Group CAT# Siliporite_Nitroxy_5 |

RESOURCE AVAILABILITY

Lead contact
Further information and requests for resources should be directed to and will be fulfilled by the lead contact, Sean M.W. Wilson (seanwilson@terrafixing.com).

Material availability
CO₂ pure gases was obtained from Linde Canada (99.99%, Burlington, ON, Canada). The Na-X (brand name Siliporite Nitroxy 5), and a Li-X (brand name Siliporite Nitroxy SXSDM) faujasite structured adsorbents were acquired from CECA (Paris, France).

The chemical compositions and structure of the samples (Table 1) were measured using energy-dispersive X-ray spectroscopy and are presented in Table 2 along with the Ar Brunauer-Emmett-Teller (BET) surface areas. Since pellets were analysed, some binder composed of silica or alumina might be present which would inflate either the silica or alumina numbers.

Zeolites used in this study

| Manufacturer | Name | Cation | Structure | Pellet |
|--------------|------|--------|-----------|--------|
| CECA Arkema Group | Siliporite Nitroxy 5 | Na⁺ | Type X | 0.6mm |
| CECA Arkema Group | Siliporite Nitroxy SXSDM | Li⁺ | Type X | 0.6mm |

*Main cation in structure.

Chemical composition of Na-X and Li-X cation atomic percentages and lattice Si/Al ratio along with Ar BET surface areas

| Adsorbent | Cation (Atomic %) | Lattice | Surface Area |
|-----------|-------------------|---------|--------------|
|           | Li⁺ | Na⁺ | Mg²⁺ | Adsorbent | Li⁺ | Na⁺ |
| Na-X      | 0 | 8.80 ± 0.45 | 0.32 ± 0.47 | 0.23 ± 0.25 | 17.49 ± 0.16 | 580 |
| Li-X      | 4.65 ± 0.50 | 0 | 2.67 ± 0.61 | 0 | 1.51 ± 0.23 | 610 |

Data and code availability
The data that support the findings of this study are available in the Supplemental Information as well as from the corresponding author upon reasonable request.

METHOD DETAILS

Minimum work required to concentrate CO₂
The minimum work required to capture and concentrate CO₂ to pure CO₂ ($W_{\min}$) is given by Equation 1. This is derived from the second law of thermodynamics which can be seen in work from APS.34
\[
W_{\text{min}} = -\frac{RT}{yM_{\text{CO}_2}}(y \ln y + (1 - y)\ln(1 - y))
\]  
(Equation 3)

Where \( R \) is the gas constant, \( M_{\text{CO}_2} \) is the molar mass of carbon dioxide, and \( y \) is the initial feed concentration of \( \text{CO}_2 \).

**Equilibrium isotherms**

The pure component isotherms of Na-X and Li-X were measured using a VTI Scientific Instruments (Hialeah, Florida, United States) GHP gravimetric system for \( \text{CO}_2 \) adsorption at 10°C, 30°C, 50°C, 70°C, and 90°C. Sorbent samples were first regenerated at 350°C under a vacuum pressure of approximately \( 10^{-5} \) atm until there was negligible weight change and their mass was recorded. Samples were then evaluated at increasing pressures of up to 6.4 atm. This was done using two pressure transducers, one from 0 to 1000 Torr with an accuracy of ± 0.25% of reading, and another from 0 to 900 psi with an accuracy of ± 0.36 psi, and a microbalance with an accuracy of ± 5 x 10⁻⁷ g. Samples were checked for hysteresis by decreasing the pressure and performing desorption data points. To correct for buoyancy, helium at similar pressure and temperatures was used. A schematic drawing of the setup is included in Figure S1.

The resulting adsorption isotherms were fitted to the Sips and Toth models using the sum of least squares method. The isotherm model with the highest coefficient of determination (R²) was used to reflect the isotherm. These isotherms were then used to analyse isosteric heat of adsorption (\( -\Delta H_{\text{ads}} \)) as a function of surface coverage (\( q_a \)) using the Clausius-Clapeyron equation (Equation 3). Specifically, \( -\Delta H_{\text{ads}} \) was calculated from the isotherm models at 10°C–90°C and pressures between 0 and 6.5 atm.

\[
\frac{(-\Delta H_{\text{ads}})}{RT^2} = \left[ \frac{\partial \ln P}{\partial T} \right]_{q_a}
\]  
(Equation 4)

**Fixed bed adsorption breakthrough curves**

Fixed bed breakthrough experimentation was used to assess the multicomponent gas behaviour in the adsorption step of the 5-step TVSA cycle. A schematic diagram is included in the Supplementary Information (Figure S2). The adsorption column’s dimensions were: 1.09 cm inner diameter, 1.27 cm outer diameter, 14.5 cm in length and had a volume of 13.5 cm³. The column was packed with Na-X or Li-X (as received from the manufacturer) and secured with quartz wool on either end. Each experiment began with a degassing step using nitrogen purge at 250°C for at least 24 h. For the adsorption step, outdoor air from Ottawa (ON, Canada) was blown at 2500 sccm through the system, and measured using a 10000 ± 100 sccm mass flow controller. This air contained 78.1% N₂, 20.9% O₂, 0.93% Ar, and 390–461 ppm of CO₂ (the CO₂ concentration fluctuated due proximity within city51). This air was dehumidified using desiccants (a layered bed of silica gel and 3A) before being fed to the adsorption column. The temperature of the input air and the column was controlled using a temperature-controlled bath between −58 and 58°C. The column temperature was measured at the inlet, outlet, and outside of the column using T-type thermocouples. The average column pressure, measured from the inlet and outlet pressure transducers (100 psia ± 0.25 psi), was between 1.20 and 1.29 atm for experiments, respectively. The exiting air CO₂ concentration was measured using a CO₂ Infrared Spectrometer (10,000 ppm ± MAX(1% of reading, 0.1 ppm)) which was vented to the atmosphere. After the CO₂ had broken through the column and reached a steady state, the column was degassed at 250°C with a nitrogen purge before further experimentation.

**Energy requirement for the 5-step TVSA cycle**

The energy requirements for a DAC technology are based on the mechanical energy and the thermal energy needs of the system. Mechanical energy is composed of three components: \( (E_F) \) for air flow through the sorbent, \( (E_S) \) for the removal of wastes and products by vacuum, and \( (E_V) \) energy to compress the product stream to 15 MPa. Mechanical energy is normally powered by electricity. Thermal energy is composed of three components: \( (E_P) \) the sensible energy required to heat up the adsorbent, \( (E_D) \) the energy required to desorb the CO₂, and \( E_{WS} \) the additional energy required to regenerate the desiccant. The thermal energy for the system can be provided by electricity powering heaters, or a heat stream such as that from a thermal solar power plant.

\( E_V \) is an important parameter when determining the energy requirement for a DAC process and can be the largest mechanical energy requirement. This is due to the low CO₂ content in air of 17.1 mmol of CO₂/m³ of
dry air (at 420 ppm of CO₂). The energy requirement for air flow can be estimated using a correlation which was derived and provided by the American Physical Society (Equation 5).

\[
E_F = \frac{P_{\text{drop}}}{\alpha T C_{\text{CO}_2}}
\]  
(Equation 5)

\[
P_{\text{drop}} = 32 \frac{\nu \mu L}{d_v^2 \varepsilon}
\]  
(Equation 6)

\[
\alpha_A = \frac{\text{Moles of CO}_2 \text{ Adsorbed during Adsorption and Pressurization Steps}}{\text{Total Moles of Gas that Entered the Column during Adsorption and Pressurization Steps}}
\]  
(Equation 7)

\[
\alpha_D = \frac{\text{Moles of CO}_2 \text{ from Evacuation step}}{\text{Total Moles of CO}_2 \text{ from Evacuation, Waterbed Regeneration, and Blowdown Steps}}
\]  
(Equation 8)

where \(P_{\text{drop}}\) is the pressure drop that can be calculated from the Hagen-Poiseuille Equation for packed beds composed of a monolith adsorbent (Equation 6), \(\alpha_T\) is the total capture fraction that was calculated as the product of adsorption capture fraction \((\alpha_A)\) (Equation 7) and the desorption capture fraction \((\alpha_D)\) (Equation 8), and \(C_{\text{CO}_2}\) is the concentration of CO₂ in the air which is 0.76 g/m³ for 420 ppm of CO₂ at 25°C and 1 atm. For the Hagen-Poiseuille Equation, \(L\) is the length of the bed, \(v\) is the superficial velocity, \(d_v\) is the diameter of the channel, \(\varepsilon\) is the void fraction in the bed.

A theoretical method can also be used to calculate the capture fraction of CO₂ during adsorption step but was not used in the calculation of energy in this study. This can be calculated from the characteristic length of the adsorbent, \(L_o\), which is similar to the concept of the mass transfer zone of a breakthrough curve shown in Equations 9 and 10.

\[
\alpha_A = 1 - \exp\left(\frac{-L}{L_o}\right)
\]  
(Equation 9)

\[
L_o = \frac{\eta \nu e d_v^2}{D}
\]  
(Equation 10)

This characteristic length can be calculated from, \(D\) the molecular diffusion of CO₂ in air which is approximately 2.1 \times 10⁻⁵ m²/s, and \(\eta\) the dimensionless separation constant which is equal to 0.068 for the case of diffusion from the gas to the surface of the pellet being slower than the diffusion from the surface of the pellet to the inside of the pellet. (Equation 11).

\[
\eta = f(D_p)
\]  
(Equation 11)

These equations condense the energy required for flow to system parameters \((\nu, L)\), and adsorbent parameters \((D_p, \varepsilon, d_v)\), allowing us to get insights into optimizing and reducing the energy for flow.

To make an approximate estimate of the energy for flow in a unit implemented in the large scale, we must specify the form of the packed bed containing the adsorbent. One approach is to use monoliths consisting of numerous parallel channels of adsorbent. This is done to reduce the pressure drop across the bed to be as low as possible. For Equation 5, this study assumes a design pressure drop of 213 Pa, and a desorption capture fraction \((\alpha_D)\) of 1.0 based on a previous study. The energy for flow can then be calculated using the adsorption capture fraction \((\alpha_A)\) from breakthrough experiments and a fan efficiency of 85%.

The mechanical energy is also composed of the energy required for the vacuum and compression. Assuming only pure CO₂ is being vacuumed from the bed, this energy cost would only be 0.0062 MWh/tonCO₂. If only pure CO₂ is being compressed, the energy for compression of the final product to 15 MPa would remain constant at approximately 0.12 MWh/tonCO₂. This assumes a vacuum pump and the compressor efficiency of 80%.
The thermal energy for the evacuation step is composed of the energy required to desorb the CO₂ along with the sensible energy to heat the CO₂ to the desorption temperature (Equation 12), and the sensible energy to heat up the adsorbent to the desorption temperature (Equation 13).

\[ E_D = \left( M_A \Delta H_A + M_S C_{PS} \Delta T \right) / a_D \]  
\[ E_S = M_S C_{PS} \Delta T / a_D \]  

where \( M_A \) is the mass of the adsorbed CO₂ species, \( M_S \) is the mass of the adsorbent, \( C_{PS} \) is the heat capacity of the adsorbed CO₂ species, \( \Delta H_A \) is the heat of adsorption of CO₂ (The average heat of adsorption of CO₂ from the Clausius-Clapeyron graph was used, Li-X = 50.8 kJ/mol and Na-X = 45.4 kJ/mol), and \( C_{PS} \) is the heat capacity of the adsorbent. To reduce the amount of thermal energy required:

- Using an adsorbent that can be regenerated at a colder desorption temperature will reduce the energy per ton of CO₂ captured.
- Using an adsorbent that can capture more CO₂ per ton of adsorbent, reduces the ratio of the mass of the adsorbent needed to be heated up versus the mass of CO₂ adsorbed, requiring less sensible energy for heating up the adsorbent per tonCO₂.
- Using an adsorbent with a lower heat of adsorption reduces the amount of energy required release the CO₂ from the adsorbent.
- Using an adsorbent with a lower heat capacity reduces the sensible energy required to heat up the adsorbent to the desorption temperature.

For the waterbed regeneration step of the process, dry air from the exit of the adsorption step is used to back flow air and carry the heat from the zeolite bed to regenerate the desiccant bed. If the amount of energy that is required to regenerate the desiccant bed is greater than the sensible energy of the zeolite bed, additional heat is added with the aid of a heater (\( E_{\text{Additional}} \)). The total energy required for the desiccation is calculated based on the energy required to desorb the H₂O from the total amount of air that entered the process. The quantity of water in the air was calculated from empirical equations in literature covering the range of -80°C to 50°C. This study uses silica gel to desiccate the bed with a heat of adsorption of 2980 kJ/kgH₂O.

**Capital costs**

One of the measurable initial capital costs for DAC technology is the capital investment for the liquid or solid sorbents. This capital cost is a function of the sorbent’s working capacity, the sorbent’s working lifetime, and the swing time of the process as shown in Equation 14.

\[ \text{Cost of Sorbent Consumption} = \frac{\text{Sorbent Cost} \times \text{Swingtime} \times \text{Working Capacity}}{\text{Working Capacity} \times \text{Lifetime} \times \text{Sorbent Cost}} \]  

(Equation 14)

Having a lower cost of sorbent consumption relative to amount of CO₂ captured is desirable and can only be achieved with high working capacities, fast cycles, and long lifetimes. High working capacities can be investigated by looking into the loadings in pure gas adsorption isotherms, with larger capacity differences over temperature and pressures indicating more desirable sorbents. Lifetime of the sorbent is harder to quantify in a laboratory, however. Lifetimes, unless degrading after dozens of cycles which has been identified in the majority of MOFs and hybrid ultramicroporous materials, are harder to measure, with amine impregnated sorbents being shown only up to 100’s of repeated cycles in the presence of water. In a similar separation as DAC, Zeolites in industry are shown to last 15 years in air separation processes.

**Sips and toth model**

Related to STAR Methods. The Sips isotherm model (Equation 15) and the Toth isotherm model (Equation 16) are commonly use to model the adsorption isotherm over the full range of pressures. These models were fitted using the sum of least squares method and the isotherm with the highest coefficient of determination (R²) was used to represent the isotherm.

\[ \frac{q_e}{q_s} = \frac{(\beta P)^n}{1 + (\beta P)^n} \]  

(Equation 15)
\[ \frac{q_v}{q_s} = \frac{\beta P}{(1 + (\beta P)^t)^{1/t}} \]  

(Equation 16)

QUANTIFICATION AND STATISTICAL ANALYSIS

Uncertainties of the equipment were used to determine the uncertainties of the reported values along with replicate runs, with the larger uncertainty being reported. For the determination of models, the sum of least squares method was used with the highest coefficient of determination being used to determine the best fitting parameters.