6

Capturing CO_2 from the atmosphere: rationale and process design considerations

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In this chapter, our aim is to provide an overview of air capture technologies that focuses on three broad topics. First, we provide an economic and technical rationale for considering direct capture of CO_2 from ambient air. Second, we describe some of the more important constraints and trade-offs involved in the design of air capture systems from the standpoint of chemical engineering and physics. Third, we provide an overview of a particular air capture technology that we are developing which combines a contactor using a high molarity sodium hydroxide solution with a titanate-cycle caustic recovery process.

6.1 Rationale: physical carbon arbitrage

Capturing CO_2 from the air at a concentration of 0.04% may seem absurd given that after roughly two decades of research and development there are still no full scale commercial power plants with CO_2 capture – for which the exhaust gas CO_2 concentrations are greater than 10% – and only a handful of large commercial pilots appear to have financing in place to move ahead.

The basic thermodynamics and physics suggest that capturing CO_2 from the air need not be much harder than post-combustion capture from a power plant (Section 6.2). It nevertheless seems clear that if an air capture plant and a post-combustion capture facility at a large electric power plant are designed and operated under the same economic conditions, that is with the same costs for construction and energy

and the same cost of capital, then the cost of air capture will always be significantly higher than the cost of post-combustion capture.

This might seem a decisive argument against air capture, but it implicitly assumes that (a) air capture is competing against capture from power plants, and (b) both kinds of capture plants will be built in the same location with the same capital and operating costs. Both these assumptions are false.

First, air capture is not likely to compete against capture from large fixed sources or power plants but rather against means of reducing emissions from mobile or small sources such as airplanes or small industrial facilities. These carbon emissions are hard to eliminate by process modification or fuel substitution while collection of the captured CO_2 would be impractical. The cost of emissions reductions and sequestration in such places can easily exceed hundreds or even thousands of US dollars per tonne of CO_2.

Second, the economic argument for air capture is all about arbitrage (Lackner 2003; Zeman & Lackner 2004; Keith *et al.* 2005). Assuming that air capture can be achieved at a modest premium above the cost of power plant capture, its defining advantages are that (a) it allows us to apply industrial economies of scale to a myriad small and hard-to-control CO_2 emitters such as aircraft and home furnaces; (b) it enables the (admittedly partial) decoupling of carbon capture from the energy infrastructure, easing the constraints that arise when new energy technologies must be integrated into the existing infrastructures; and (c) it provides the (partial) freedom to build a capture plant where it is cheapest or near the best sequestration sites.

An economic carbon market allows efficient allocation of the cost of emitting carbon to the atmosphere. Compared to command-and-control regulation, the flexibility of a carbon market allows greater economic efficiency. An ideal carbon market allows carbon mitigation to follow the global supply curve starting with the least expensive options and moving upwards towards the most expensive. In combination with the carbon market, air capture allows carbon to be physically removed in the most cost-effective circumstances, eliminating – in theory – the necessity for controlling the most expensive sources (such as aircraft) even if it is necessary to reduce net carbon emissions to zero. We call this attribute of air capture *physical carbon arbitrage* distinct from the arbitrage achievable by carbon markets.

Consider some of the driving cost differences:

- The capital cost of building the same large energy infrastructure varies by factors of two to four between low-cost locations like China and expensive places like Alberta, Canada.
- The cost of energy needed to drive the capture process varies enormously between, for example, commercial natural gas in Europe and stranded gas in a remote location or coal.

- The cost of CO$_2$ disposal ranges from essentially infinite in locations far from adequate reservoirs or without regulatory regimes that allow storage to negative costs of order 25–50 \$/tCO$_2$ if CO$_2$ is delivered to large oilfields suitable for enhanced oil recovery.
- While the design of air capture facilities will necessarily vary somewhat depending on local factors, it seems likely that designs could be substantially more standardized and therefore less expensive than is typical for large energy infrastructure. This same argument applies to the individual equipment items that might be used in a standardized process.
- Free-standing capture systems can be made as large as desired and do not have to match the CO$_2$ output of any particular facility. This is especially important for relatively small CO$_2$ sources such as small factories. Based on the rule of thumb that process plant capital costs scale as roughly the six-tenths exponent of capacity, building a single large plant of 100 units capacity costs about 16% as much as 100 small plants of unit capacity.

There is also a less tangible benefit of air capture. Construction of air capture plants in remote or underdeveloped areas can also be a form of economic development, creating long-lasting, skilled jobs. If such development was desired for sociopolitical reasons, air capture provides an environmentally valuable option.

Large-scale technologies for capturing CO$_2$ directly from the air would fill a crucial hole in the toolbox of carbon-climate technologies. Air capture breaks the link between emission source and capture technology; it enables carbon-neutral hydrocarbon fuels (CNHCs, see Section 6.6 and Chapter 7) made from the captured CO$_2$; and in the long run, it enables negative emissions as a tool to manage global climate risks.

6.2 Physical and thermodynamic constraints

While any individual air capture technology will face a host of engineering challenges, there are two fundamental factors that make air capture more difficult than conventional post combustion CO$_2$ capture processes: first, the energy and materials cost of moving air through an absorber, and second the thermodynamic barrier due to the low concentration of CO$_2$ in air. In this section we describe the physics that constrains an idealized air capture system with respect to these two factors.

There is no lower bound to the energy required to move air through an absorber. The energy required to move air can be made arbitrarily low if the speed of air through the absorber approaches zero. However, there is a strong trade-off between this energy cost and the capital cost of the absorber. As the flow velocity approaches zero, the rate of capture per unit absorber surface will also approach zero; so while energy costs approach zero, the amortized cost of capital will approach infinity. This is because each unit of absorber structure captures CO$_2$ at a rate that approaches zero yet still has a finite cost for amortizing the capital required for its construction

along with the cost of maintenance to keep it operational. Any practical design must balance the cost of energy required to drive air through the absorber against the cost of capital and maintenance.

If we make a reasonable – though not universally applicable – assumption that the flow through the CO_2-absorbing structure is laminar, then the energy required to drive air through the absorber and the capture rate are linked by the fact that – for laminar flow – the transport of both CO_2 and momentum are diffusive processes that occur in a fixed ratio.

Neglecting factors of order unity that depend on the specific geometry, we can compute the energy required as compression work to capture a unit of CO_2 in a laminar-flow absorber made from a substance that is sufficiently absorptive that the uptake rate is limited by CO_2 transport in air (air-side limited). Under these assumptions, the specific energy per unit CO_2, E, is

$$E = \frac{1}{r\rho_{CO_2}} \rho V^2 \frac{\nu}{D}$$

where air has density ρ, velocity V and kinematic viscosity ν; and CO_2 has diffusion constant D, density ρ_{CO_2} and mole fraction r. For air at standard conditions with 400 ppm CO_2 at an air velocity of 10 m/s, the minimum energy is 0.15 GJ/tCO_2.

This result can be obtained in a physically intuitive way by thinking about a parcel of air that moves through a structure coated with a perfect CO_2 absorbing material. As the parcel moves, gas molecules contact the surface by diffusion, transferring momentum to the surface and losing CO_2. When the parcel has travelled far enough that most of the CO_2 has been absorbed it will also have transferred most of its initial momentum to the surface, which would be sufficient to bring the parcel to a stop if there were no pressure gradient sustaining the flow. The minimum pressure drop needed to capture a minor constituent gas in a perfect laminar absorber is therefore, to order unity, the stagnation pressure at the flow velocity, that is, $\Delta p_{min} = \frac{1}{2}\rho V^2$ scaled by the ratio of diffusion rates which itself is the ratio of relative concentrations of momentum or CO_2 and their transport coefficients.

The thermodynamic minimum energy required to separate CO_2 from the air is given by the free energy of mixing,

$$RT \ln\left(\frac{p}{p_0}\right),$$

where p is the final pressure of pure CO_2, p_0 is the initial partial pressure, R is the ideal gas constant and T is the working temperature. (Note that this formula ignores the change of free energy of the air when CO_2 is extracted, a $\sim 1\%$ correction.) At a 20 °C operating temperature the minimum energy required to capture CO_2 from the atmosphere at 400 ppm and deliver it at one atmosphere is 0.43 GJ/tCO_2.

Now, consider the comparison between capturing CO_2 from the air and from the exhaust stream of a coal-fired power plant assuming that the CO_2 is to be delivered in compressed form suitable for pipeline transport at a pressure of 150 bar. A process which captures CO_2 from the air can, in principle, trade off the cost of scrubbing a larger fraction of CO_2 from the air against the cost of moving additional air if the fraction captured is smaller. In practice, the fraction captured will depend on a complex optimization between capital and operating costs. Suppose that half of the CO_2 is captured and thus that CO_2 must be removed from air at an average concentration of about 300 ppm and, for the last molecules captured, a final concentration of 200 ppm. Assuming the worst-case 200 ppm requirement for all the capture, the minimum energy to go from 200 ppm to 1 bar is 0.47 GJ/tCO₂ and the minimum energy cost of compressing CO_2 from 1 to 150 bar is 0.28 GJ/tCO₂ for a total of 0.75 GJ/tCO₂.

Most designs for post-combustion capture from power plants assume that at least 90% of the CO_2 must be scrubbed from the exhaust gases with a representative concentration of 15% CO_2. Again, what matters is the minimum energy to capture the final bit of CO_2 from exhaust gases at 1.5% or 15 000 ppm for which the minimum energy is 0.23 GJ/tCO₂ and, counting the same compression cost to 1 bar, the total minimum energy to deliver it at 150 bar is 0.51 GJ/tCO₂.

Comparing CO_2 capture from air and power plant exhausts, the intrinsic thermodynamic penalty due to the lower starting concentration of CO_2 in air is therefore about a factor of 2 if the product is a 1 bar pure CO_2 stream and a factor of about 1.5 if the product is pipeline pressure CO_2. These ratios move towards a factor of 1.0 as the percentage capture of CO_2 increases; however, the energy cost per ton of CO_2 increases simultaneously. The primary reason to move in this direction is the possibility of building and operating smaller air-contacting equipment because not as much air must be treated to capture the target tonnage of CO_2.

In practice, proposed designs for both air capture and post-combustion capture are a long way from thermodynamic efficiency limits. Aqueous amines, the most commonly considered method for post-combustion capture require about 2–3 GJ/tCO₂ of regeneration heat (IPCC 2005; Rao *et al.* 2006) and the NaOH solutions which we are exploring for air capture have a thermodynamic minimum regeneration energy of 2.4 GJ/tCO₂.

The physical limits are, nevertheless, an important guide to the development of energy technologies (Keith *et al.* 2005):

These thermodynamic arguments do not, of course, prove that practical air capture systems can be realized, nor is the performance of air capture technologies likely to approach thermodynamic limits in the near future. The ultimate thermodynamic limits are nevertheless an important basis for suggesting that air capture can be achieved at comparatively low cost. From the liberation of pure metals from their oxides to the performance of internal

combustion engines, electric motors and heat pumps, the historical record strongly supports the view that thermodynamic and other physical limits serve as an important guide to the long run performance of energy technologies.

6.3 Process design considerations for the primary gas separation step

6.3.1 Physical separations

Physical separation processes are among the most widely used gas separation techniques in chemical engineering, but most of them can be ruled out almost immediately because of the burden of processing the non-CO_2 components of air. Physical separations typically depend on temperature or pressure variations, yet the dilute concentration of CO_2 makes direct application of these techniques impractical. Heating air by 1 °C or pressurizing it by 1000 Pa (1% of an atmosphere) both require approximately 1.5 GJ/tCO_2, about three times the thermodynamic minimum energy required for separating CO_2 from air to produce a 1-bar product; yet a temperature swing of 1 °C or a pressure swing of 1000 Pa are still grossly insufficient to drive common physical separation process. This 1.5 GJ/tCO_2 also corresponds to the net energy input if there is a very high 95% energy recovery on a still-modest 20 °C temperature swing or 20 kPa pressure swing.

Cryogenic separation

CO_2 could be recovered by cooling air at 1 atmosphere pressure to the point that CO_2 condenses as a solid. At a 400 ppm concentration, this requires an initial temperature near -160 °C and requires cooling not only the CO_2 but also the mass of oxygen and nitrogen too. Conceivably the air could be maintained above the 0.53 MPa (approximately 5 atm) triple point pressure while being cooled so the CO_2 can be recovered as a liquid from the system, perhaps after distillation of a condensed nitrogen/oxygen/CO_2 mixture. While this type of liquefied gas processing is established technology, cryogenic separations are expensive. Moreover, since the whole air mass must be cooled, an order of magnitude estimate for the cost for capturing CO_2 may be derived from the cost of cryogenic O_2 separation using the 500 : 1 ratio of O_2 : CO_2 in ambient air implying an energy cost for CO_2 capture of many hundreds of GJ/tCO_2.

Physisorption

Physisorption to a solid surface, for instance a molecular sieve, is currently used in the front end of air separation plants to remove CO_2 and water to prevent them freezing out in the later cryogenic distillation. Adapting such a process for air capture would require overcoming significant problems such as preferential

absorption of water over CO_2. Moreover, both pressure-swing and temperature-swing adsorption are batch processes with inefficiencies in recovering the energy required to swing the beds and their contents through their operating cycles. The mechanics of moving extremely large quantities of air through packed beds of solids also presents a major design problem, since having large amounts of surface area to improve mass transfer rates also means large areas for momentum loss, i.e. pressure drop.

Membranes

Membranes that separate CO_2 on the basis of its molecular size or its solubility in the polymeric matrix are under active development for application to flue gases (IPCC 2005). Using them to separate CO_2 from air where the driving force for CO_2 is at most 40 Pa seems implausible given the relatively low molecular fluxes through membranes. Increasing the CO_2 driving force by pressurizing the air feed is not practical because of the capital costs of compression and the energy losses in recovering that compression work. Operating the downstream (CO_2 collection) side of the membrane at vacuum conditions does not increase the 40 Pa driving force and therefore the flux because that value already assumes zero pressure on the collection side of the membrane. Alternatively, the membranes could pass oxygen, nitrogen and argon while leaving concentrated CO_2 behind. This approach requires a tremendous membrane area because of the quantity of gases that must be transmitted, the last fraction of which has little driving force because of its low residual concentration in the CO_2.

Gas centrifuges

Gas centrifuges suffer from low throughputs and relatively low separation per stage, problems which are worsened by the complexity of the equipment in each separation stage. Further, advances in design and operation of these systems are subject to government classification and export control limitations because of their potential use to separate and enrich nuclear materials.

Physisorption into a liquid

Physisorption into a liquid is the basis for processes that absorb CO_2 into a simple solvent such as cold methanol. Applying them to air capture suffers penalties with incomplete energy recovery while cooling and reheating the air stream and with the costs of any volatility loss of the solvent to the extremely large flow of air through the system.

6.3.2 Chemical separations

While other methods are no doubt possible, in practice most existing air capture development is focused on two broad separation methods, chemisorption in aqueous solutions and chemisorption on solid surfaces.

Aqueous absorption

Separations that take advantage of CO_2's acidity in solution are the current standard for industrial processing. Literally dozens of such processes and solvents have been developed for the removal of CO_2 and H_2S (collectively called acid gases) from natural gas, either separately or as a mixed gas stream. These processes have more recently been used for treating synthesis gas mixtures from gasification of coal, natural gas, or heavy petroleum fractions (IPCC 2005). These processes differ functionally from each other in their selectivity for CO_2 against H_2S; their ability to remove these gases to very low (ppm or lower) levels; their sensitivity to other gases such as ammonia; their maintenance and operating costs; and their trade-off of capital and energy costs.

The primary barrier to using such a process is that the kinetics of CO_2 dissolution into water are limited by the initial reaction to form carbonic acid ($CO_2 + H_2O \rightarrow H_2CO_3$). While this reaction is sufficiently fast to make aqueous systems cost-competitive for capture of CO_2 from power plant exhaust streams, it is too slow at the much lower concentrations in ambient air. Two methods are being explored to get around the kinetic limitation in aqueous systems.

One option is to accelerate the reaction using a catalyst. The naturally occurring enzyme carbonic anhydrase can accelerate the $CO_2 + H_2O$ reaction by a factor of $\sim 10^9$ and facilitates respiration in living cells by catalysing the reverse reaction (all catalysts speed their target reactions in both directions). Using an enzyme as a catalyst is challenging because, to name only a few issues, they only operate in a narrow pH and temperature range and as organic compounds they may be decomposed by micro-organisms (Bao and Trachtenberg 2006). Roger Aines and collaborators at Lawrence Livermore National Laboratory are developing synthetic catalysts that would be somewhat less effective in accelerating the reaction than carbonic anhydrase but which could be tailored for the air-capture application (Aines & Friedmann 2008).

An alterative to catalysis is to use aqueous solutions with very high pH. For example, our group has focused on using NaOH solutions with a concentration between 1 and 6 mol/L with pH near 13. In these solutions the kinetics are dominated by the direct reaction with the hydroxyl radical ($CO_2 + HO^- \rightarrow HCO3^-$), which enables mass fluxes of ~ 3 gCO_2/hr-m^2 for the applicable case in which mass transfer is liquid-side limited. The advantages of strong bases are that (a) they

use simple inorganic chemistry which is insensitive to contamination, (b) vapour pressures are low so evaporative loss of the base to the atmosphere is minimal, (c) their high molarity enables low liquid-side fluid pumping work, (d) at sufficiently high molarity evaporative water loss can be eliminated, and (e) the technique does not depend on the development of novel solids or catalysts.

The primary disadvantage is the difficulty of regenerating the resulting carbonate solution back to hydroxide. Recovery of NaOH from Na_2CO_3 is closely related to 'caustic recovery', one of the oldest processes in industrial chemistry. In Kraft pulping for paper making, wood is digested using sodium hydroxide to liberate cellulose and produce pulp. The remained solution, so-called 'black liquor', consists of mainly other organic material originated from wood (e.g. lignin) along with sodium carbonate. The standard process for recovering NaOH from Na_2CO_3 depends on a calcium cycle, a process that has been used on a continuous basis for more than 80 years. Several studies have investigated adaption of this process to recovery of NaOH for air capture (Zeman & Lackner 2004; Keith *et al.* 2005; Baciocchi *et al.* 2006), alternative caustic recovery methods include the titanate cycle (Mahmoudkhani & Keith 2009).

Sorption into solids

Using an alkaline solvent, typically an organic amine compound, allows good selectivity and solvent loading without excessive regeneration costs. However, for air capture any evaporative loss of solvent to the air stream is a significant loss compared to the amount of CO_2 captured and will make the overall economics untenable. The same type of chemistry used in aqueous absorption processes can be adapted to solid sorbent phases which will not evaporate. A high surface area material can be chemically modified so that it reacts with CO_2 and can remove even low concentrations from air. The challenge then is to provide a large surface area for CO_2 capture without having a large mass of solid support which must be heated to drive off the bound CO_2.

Two solid sorbent systems are being actively developed for air capture. Both processes offer the advantage of low regeneration energy. Klaus Lackner and collaborators at Global Research Technologies (GRT) are developing an ion exchange membrane which captures CO_2 using a carbonate to bicarbonate swing driven by changes in humidity. A significant challenge is that the partial pressure of CO_2 achieved during the regeneration phase is only about 0.1 bar, so to obtain pure CO_2 suitable for sequestration it is necessary either to purge all the air from the sorbent beds (including the internal pores of the sorbent material) before performing the regeneration step in a vacuum, or to regenerate in air and then capture the CO_2 from air at a 10% concentration. Large-scale vacuum operations, especially

repeated batch processes, present a variety of engineering issues with sealing and with the generally low energy efficiency of vacuum pumping systems.

An alternative solid sorbent system is being developed by Peter Eisenberger and Graciela Chichilnisky of Global Thermostat, using solid amines on a mesoporous silica substrate similar to those that are being developed for CO_2 capture from power plants (Gray *et al.* 2007). Capture is accomplished using temperature-swing regeneration driven by low-grade heat ($\sim$100 °C or less).

In general, these solid sorption methods offer the potential to achieve low capture energies with minimal water loss. Perhaps the central challenge in commercializing them is the need to build a solid surface with very high surface area at low manufacturing cost while simultaneously achieving long service lifetimes when operating in the free atmosphere which will inevitably be contaminated with various trace chemicals and windblown dust.

6.3.3 Energy integration and energy supply

In general, a direct air-capture process will require electrical power to drive systems such as fans and pumps as well as the thermal input to drive the regeneration process itself. For a stand-alone air-capture system, thermal power could in principle be supplied by a wide range of energy sources including solar thermal power, natural gas, coal or nuclear heat. Electrical power could be imported from the grid or (co-)generated on site depending on economics and the opportunities for heat integration.

Solar offers zero energy cost and no CO_2 production but at the expense of relatively high capital costs and intermittent operation which does not integrate well with the desired steady operation of chemical processes. Because the plant would not operate at full capacity for a large fraction of the time, this raises the capital costs per ton of CO_2 collected. While it is possible to reach high temperatures ($>$1000 °C) in solar furnaces, most of the commercial development of solar thermal electricity is now focused on parabolic troughs which produce lower grade heat. Nikulshina *et al.* (2009) have explored the use of solar furnaces for $CaCO_3$ (limestone) calcination as part of an air-capture process, and such solar kilns could also be applied to the titanate process we describe below (Section 6.5).

In general, natural gas combustion offers the simplest and lowest capital cost plant design at the expense of relatively high energy costs. Combustion gas turbines offer the possibility of efficient cogeneration of power and process heat. Because our air-capture approach needs substantial quantities of high-grade heat and we wish to minimize initial technical risk, all of our current design efforts focus on natural-gas-driven systems using cogeneration so that the plant has no significant external electricity demand. We do note however that large air-capture plants, like

any large chemical process, will operate for long periods at steady high rates; this situation is analogous to base-load electrical power production where coal and nuclear systems have proven to be the most economical technologies. Where cost-effective, CO_2 emissions from the natural gas combustion in the process are captured using either oxy-fuel combustion or post-combustion capture.

Coal offers low energy cost but requires integrated carbon capture. The simplest technical approach for supplying high-grade heat to a calcination process would be direct combustion of coal with the material to be calcined (e.g. $CaCO_3$ or titanates). This process is widely used for lime production. The disadvantage is the management of the coal ash and the possibility that the ash interferes with process chemistry once the lime or titanates are cycled back into the capture process. Alternatively, coal could be used in a gasification system to supply syngas or hydrogen to heat the air-capture process, with CO_2 capture and storage for the CO_2 emissions from gasification.

Nuclear heat offers high capital and low operating costs without generating additional carbon dioxide, but it has some disadvantages beyond the well-known issue of local public acceptance. One is the requirement to manage design standards and safety engineering in the integrated plant, because different engineering standards apply to chemical/thermal and to nuclear systems. This primarily affects the documentation and engineering analyses needed to license the nuclear plant for this integrated operation. A second disadvantage is the potential operational difficulty of running a nuclear plant closely coupled to a chemical facility. This concerns economic performance rather than safety performance. Almost all existing commercial nuclear plants have been used for electrical power production, some with modest cogeneration of heat for local district heating. In operating the first of any new technology such as nuclear-powered air capture, there is always the possibility of unexpected maintenance needs or poor performance.

6.4 Operational and environmental constraints

In this section we examine operational and environmental constraints. While many of the issues discussed would apply to any air capture technology, others are specific to the large-scale strong-base system we are developing.

6.4.1 Transport issues

In addition to the capture and recovery chemistry, there are problems in moving the great quantity of air which must be processed. Consider a facility that captures 1 $MtCO_2$/yr. This value has been used in our work for the nominal full-scale plant in part to match the scale of some unit operations in current industrial

practice, and because a large capacity is needed to make progress against total global emissions. Current commodity chemical plants for products such as ethylene/propylene, ammonia and methanol (as well as coal-fired power plants) are already being built at this scale. Assuming 400 ppm CO_2, 50% capture, and 90% annual availability of the capture system, the system would have to process 500 million kg/hr of air, or 6.5 million m^3/min, or a cubic kilometer of air at standard conditions in about 2.5 hours.

This amount of air could be moved by either natural draft or forced draft using low-head fans. In either case, in the absence of an ambient wind of greater velocity than the flows into or out of the air capture plant, there would be a tendency for the air capture facility to recirculate low-CO_2 effluent air to its intake. This condition sets the facility scale. Assuming a typical wind velocity of 5 m/s, about 20 000 m^2 of intake area – or a square 150 meters on a side – is needed to collect the necessary amount of air. It is plausible to imagine a facility comparable in size to an open-roof sports stadium or, more likely, a number of separate smaller air contacting units all feeding a CO_2-rich sorbent liquid to a central CO_2 recovery facility.

Restricting air-side pressure drops to the stagnation pressure $\rho V^2/2$ obtainable without external energy input corresponds to operation at a pressure drop in the range 50–150 Pa. We can imagine developing this pressure difference through a combination of near-stagnation pressure at the inlet and a reduced pressure in a venturi or aerofoil system at the exhaust point, or we may consider it to be an initial estimate of the head to be developed by whatever type of wind-augmenting fan system might be used.

While this pressure drop is low, it is in the range of other large industrial systems. Chemical plant distillation towers designed for vacuum conditions use low-pressure-drop packing (filling material to increase the surface area of gas–liquid contact) to minimize the pressure and temperature at the bottom of the column and therefore the degradation of thermally sensitive chemicals. Evaporative cooling towers perform a mass- (and heat-) transfer function similar to a CO_2 absorber and have been built at very large scales. Windmills demonstrate that several megawatts of useful work can be recovered from a moderate wind from a swept area similar to the intake area of the air-capture plant. This energy is available to move air through the contacting system and is probably best tapped as the original kinetic energy rather than as converted electricity. This value also suggests the magnitude of fan work that would be needed to maintain production on windless days.

The large amount of air to be handled also affects the amount of sorbent liquid which must be circulated and brought into contact with the air. If a conventional countercurrent contacting system were to be used, there would be a significant energy penalty for lifting to the top of that contactor an amount of liquid which is of similar order of magnitude as the mass of air to be processed. That lifting work

cannot be recovered because the liquid remains at one atmosphere pressure (i.e. does not develop any elevation head) as it falls freely down over a packing material which spreads it into thin layers and streams with a large surface area (note that the mixing of these layers as they flow moderates a decline in the absorption rate as the surface liquid becomes saturated with CO_2). In our exploration of contactor operation we have found that continuous liquid circulation is not necessary, and that periodic pulsed addition of sodium hydroxide sorbent solution to the top of the contactor is sufficient (Section 6.5).

6.4.2 Operational issues: environmental

An air-capture system must not only perform well at the design conditions but must be designed to be robust to a variety of external influences. Perhaps the most obvious of these are the local atmospheric conditions. The contactor will take in enormous amounts of air. If it is raining or snowing, some amount of liquid water will come with the air and in a thunderstorm or tropical storm this amount could be substantial. Even when it is not raining the water balance is important. Except in the coincidence that the water fugacity in the caustic sorbent solution equals the partial pressure of water in the atmosphere, the system will either extract water vapour from the atmosphere or will evaporate water into the air stream. Both possible situations must be compensated for since the trend might continue for several days or weeks.

Two types of freezing problems must be considered. Temperatures below $0\,^\circ$C will freeze pure water, creating icing problems in the air intake system if it collects rain, snow or condensation. Colder temperatures run the risk of freezing the sorbent liquid or causing the dissolved caustic to precipitate if its saturation temperature is reached. As one easy solution, air-capture systems could be located only in semitropical or tropical areas.

Performance of the air-capture system will depend on atmospheric pressure because this affects both the partial pressure of CO_2 – and therefore the driving force for capture – as well as the density of air and consequently the volume that must be moved to bring a certain amount of CO_2 into the absorber. Normal fluctuations in atmospheric pressure and water vapour pressure (absolute humidity) each have a total range on the order of 3% of the total pressure and do not pose a major problem since these differences should be within the normal design conservatism. More important is the elevation at which the air-capture system is installed. At an example elevation of 1400 m, air pressure is about 85% of the value at sea level. This suggests that low elevation siting is preferable although that also corresponds in many places to greater population densities. Air density will also change with the local temperature. Depending on the location, seasonal absolute temperature

changes can be up to about 20% and the resulting density changes will affect plant performance throughout the year.

6.4.3 Operational issues: contaminants and emissions

A system designed to recover a component of air present at about 400 ppm, such as CO_2, also has the potential to recover other species present at ppm levels. Such unintended species must either be innocuous in the system or they must be specifically considered in the design. If the basic process discharges only pure CO_2, other purge streams must be added to remove problematic low-concentration air contaminants to prevent their continual accumulation in the process.

The chemistry of capturing the acid gas CO_2 will naturally lead to capture of other acid gases such as SO_2, NO_x, and, if present, H_2S. Solid sulphates present as aerosols could also be captured. The build-up of these materials must be understood to prevent formation of sulphate or other precipitates. However, this incidental capture creates an opportunity to generate SO_x or NO_x removal credits which might conceivably contribute to the overall process economics.

The atmosphere, especially near the ground, contains suspended particulates. Collecting and purging inert solids or tar and soot particles from vehicle exhaust is not difficult. The bigger problem is likely to be materials somewhat soluble in caustic solutions like silicate compounds which might dissolve, accumulate and eventually precipitate elsewhere in the process.

A related problem is capture of biological contamination such as wind-blown pollen, seeds, leaves, insects or birds. Unless screens remove these objects, their organic molecular constituents could be decomposed by the caustic sorbent and accumulate in the sorbent loop. One resulting concern is hydrolysis of lipid molecules (fats and oils) to form soap which would create either foam or a solid scum build-up.

Finally, the air contactor might be expected to generate its own emissions issues. The reduced CO_2 concentration in the effluent plume will hinder plant growth in the region downwind of the capture facility. This might stress natural vegetation leading to ecological changes and in the case of planted crops could create economic damages. Depending on the changes to the temperature and humidity of the air as it passes through the contactor, the effluent plume might be denser than the local atmosphere and have a tendency to remain near the ground. At a wind speed of 5 km/hr under stable conditions the plume recovers to 90% of upwind CO_2 concentration within 2 km. Under unstable conditions or faster flow velocities recovery is much faster.

The facility air effluent, especially at night when the atmosphere is cooler, might also form a large fog plume because of its water vapour content. This phenomenon

Table 6.1 *Power to drive the air at various velocities*

Velocity (m/s)	Pressure drop (Pa)	Compression work (W)	Capture rate (tCO$_2$/yr)	Power input (kWh/tCO$_2$)
0.9	25	23	7.7	24
1.2	37	45	9.1	39
1.5	42	63	9.9	50

is identical to what happens in conventional cooling towers but will be of greater scale. Its potential effect on visibility for automobile and aeroplane traffic, as well as on those individuals living or working in close proximity, must be considered.

The extremely large volume of air can still lead to downwind problems even if concentrations of effluent emissions are quite low. Two that must be evaluated are the emission of aerosolized caustic droplets and the possible release of malodorous ammonia vapour generated by protein degradation in the high pH sorbent solution.

6.5 An example

We are currently developing an air-capture process based around NaOH capture with a titanate-based hydroxide regeneration system (Keith *et al.* 2005; Stolaroff *et al.* 2008; Mahmoudkhani & Keith 2009). This is a multistep chemical process with many components similar to or identical to existing components used in current chemical processes.

The first step in the process is a system that contacts a strong hydroxide solution with atmospheric air, referred to as the contactor. This device will accomplish its task using structured packing similar to the material found in packed towers that are used in many chemical processing plants, but with a few key differences. The first is scale; in our current conceptual design, for example, a 1 MtCO$_2$/yr facility requires 13 contacting units 20m tall × 200m long. Second, unlike a traditional packing-based system, the contactor will be cross-flow (the liquid flowing perpendicular to the air) to reduce the maximum velocity to which the air must be accelerated and thus the energy needed to drive the air. Third, the contactor is operated in an intermittent wetting mode in which the packing is supplied fresh sorbent only a fraction of the total operating time, with sorbent hold-up allowing continued CO$_2$ collection between these times.

Regarding the use of a commercial packing in cross-flow, some experimental data are shown in Table 6.1. All values in the table are scaled to 1 square meter of intake surface. The values are taken from experiments performed during the summer of 2008 and are representative of Sulzer 250X packing with a total thickness of 1.54 m.
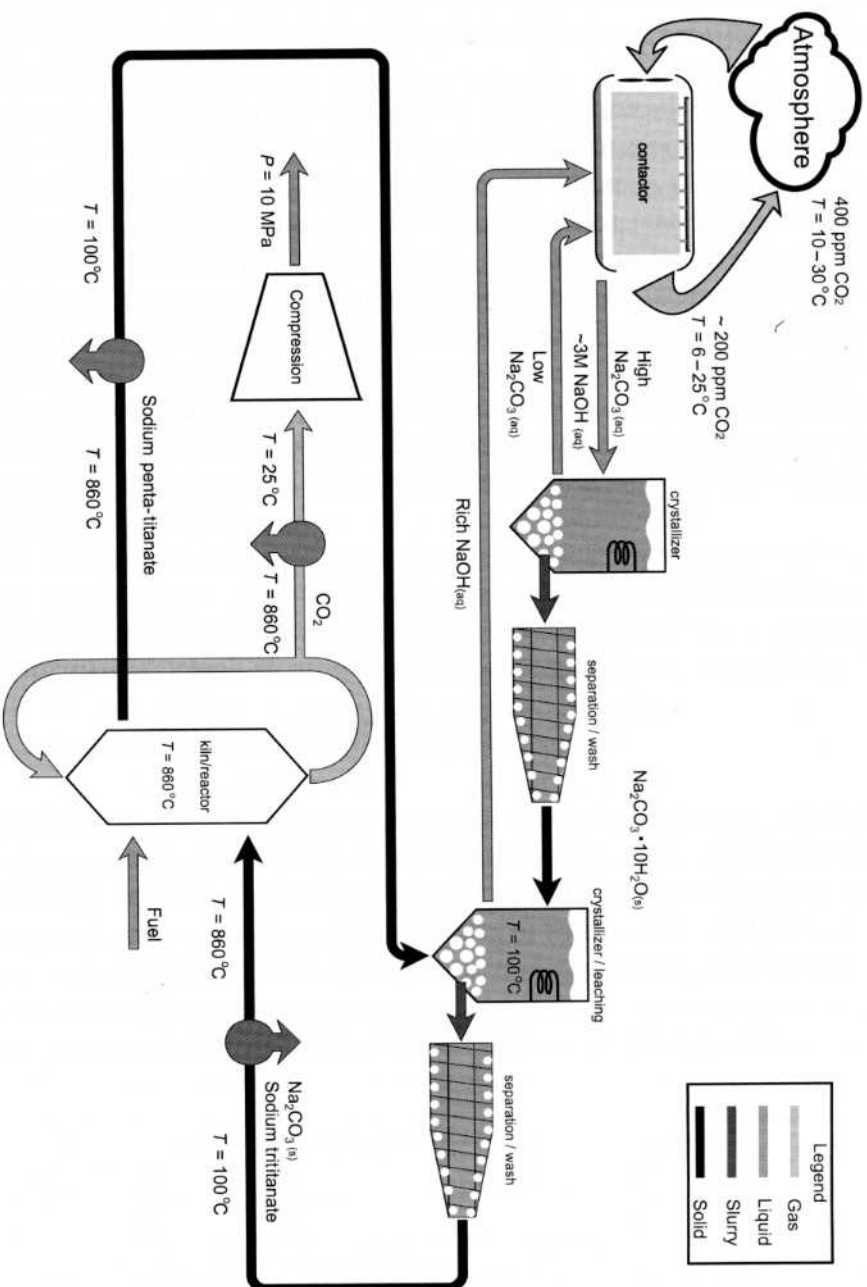
Figure 6.1 Flowsheet of a NaOH–titanate-based air-capture process. The kiln is depicted with a CO_2 recycle loop which may or may not be used depending on the kiln configuration. The solid circle-arrow symbols show major points of heat addition or subtraction (Mahmoudkhani & Keith 2009) (see also colour plate).

Table 6.2 *Heat balance and exergy for a titanate-based NaOH recovery system. Note the large enthalpy change in the titanate compounds (Mahmoudkhani & Keith 2009).*

	Enthalpy Change ΔH (kJ/mol-CO$_2$)	Temperature Range (°C)	Exergy Change ΔC (kJ/mol-CO$_2$)
Crystallizer			
Crystallization of Na$_2$CO$_3\cdot$10H$_2$O	−68.8	10	1.7
Combined Crystallizer/ Leacher Unit			
Heating Na$_2$CO$_3\cdot$10H$_2$O	8.8	10 → 31	1.9
Dissolution of Na$_2$CO$_3\cdot$10H$_2$O	67.9	31	−1.2
Crystallization of Na$_2$CO$_3$	45.3	103	−8.3
Leaching Reaction	15.2	103	−1.3
Heater			
Heating Na$_2$CO$_3$	123.4	100 → 860	93.4
Heating Sodium Trititanate	146.9	100 → 860	84.0
Reactor			
Decarbonization Reaction	65	860	−33.8
Cooler			
Cooling CO$_2$	−40.7	860 → 25	−22.1
Cooling Sodium Pentatitanate	−213	860 → 100	−129.1
Total	150		

Any change in geometry of the packing or thickness will change the values. Note that the data seem to indicate that lower air velocity is less expensive to operate, but it does not take into account the capital cost of a capture system. When the capital cost is taken into account the optimal air velocity may be higher than shown here.

The other process steps are shown in Figure 6.1 and will not be explored in depth here as they each have many analogues in current industrial practice. The thermodynamics of the idealized system are listed in Table 6.2.

A titanate-based hydroxide regeneration process has a number of advantages and a number of disadvantages when compared with the standard calcium-based process.

Advantages:

• Lower high-temperature heat requirement, 90 kJ/mol-CO$_2$ vs. 179 kJ/mol-CO$_2$ for a calcium process.
• More concentrated NaOH solutions can be generated, the calcium process is limited to one-sixth the output concentration of the titanate process.
• Elimination of calcium which may cause fouling in the contactor.

Disadvantages:

- Contamination or degradation of titanate particles must be carefully controlled.
- Heat recovery from solids is very important, since large masses of titanate particles must be heated and cooled cyclically.

When comparing the two processes it is difficult to determine which method will cost less per tonne of captured CO_2 because, although the titanate process has lower energy requirements, it has some added complexities. These will probably manifest themselves as extra capital cost and inefficiencies in heat integration, both of which increase the cost per tonne of captured CO_2. The two processes will probably be similar in cost and it will require more work to determine the preferred regeneration method for the air-capture system.

6.6 Discussion

It is technically possible to capture CO_2 from air at industrial scale. Indeed, technologies for industrial air capture were commercialized in the 1950s for pretreating air prior to cryogenic air separation. The cost of air capture is, however, uncertain and disputed. Some have argued that the costs would be prohibitively high (Herzog 2003) or that investing funds into research on air capture is a mistake because it diverts attention from more important areas (Mark Jacobson as quoted in Jones 2008). In sharp contrast, others have argued that air capture might be comparatively inexpensive and that it could play a central role in managing carbon dioxide emissions (Pielke 2009).

Our view is that air capture is simply another large chemical engineering technology. Its cost will depend on the technology employed, as well as the cost of materials, labour and energy. The economics of the process will determine its feasibility but will not be well defined until more work has been done on specific processes. As with other significant climate-related energy technologies it will not be possible to determine the cost with precision by small-scale academic research. Instead, costs will only become clear through pilot-scale process development and through costing by contract engineering firms with relevant expertise.

In our view, such development is justified for three reasons. First, early estimates suggest that the CO_2-abatement cost of air capture is less than other technologies that are getting very large research and development investments. For example, the cost of cutting CO_2 emissions by displacing carbon-intensive electricity production with roof-mounted solar photovoltaic panels can easily exceed 1000 $/tCO_2$. We are confident that a straightforward combination of existing process technologies could achieve air capture at costs under 1000 $/tCO_2$. Indeed, neither we nor others working in this area would be commercializing these approaches if we were not

able to convince investors that we could develop technologies to capture CO_2 from air at costs many times less than 1000 \$/tCO_2.

Second, air capture offers a route to making carbon-neutral hydrocarbons fuels (CNHCs) for vehicles by using captured CO_2 and clean energy sources to make synthetic fuels with desirable handling and combustion properties. Deep reductions in emissions from the transportation sector will require a change in vehicle fuel. Each of the three leading alternative fuel options – electricity, biofuels and hydrogen – face technical and economic hurdles which preclude near-term, major reductions in transportation emissions by using these technologies. Carbon-neutral hydrocarbons represent a fourth, fundamentally different alternative, a method for converting primary energy from sources such as solar or nuclear power into high-energy-density vehicle fuels compatible with the current vehicle fleet. As stated in Zeman and Keith Chapter 7, this volume:

We argue for the development of CNHC technologies because they offer an alternate path to carbon neutral transportation with important technical and managerial advantages. We do not claim that CNHCs are ready for large-scale deployment or that they will necessarily prove superior to the three leading alternatives. We do argue that they are promising enough to warrant research and development support on a par with efforts aimed at advancing the alternatives.

Finally, air capture allows negative global CO_2 emissions. While the prospect of achieving negative global emissions is distant, it is important because it represents one of the few ways to remediate human impact on climate. Without the ability to take CO_2 out of the air, the climate change arising from current emissions is essentially irreversible (Solomon *et al.* 2009).

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