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CO_2 capture from ambient air: An example system

Joshuah K. Stolaroff Greg V. Lowry David W. Keith

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Abstract

In order to mitigate climate change, deep reductions in CO_2 emissions will be required in the coming decades. Carbon capture and storage will likely play a large role in these reductions. As a compliment to capturing CO_2 from point sources, CO_2 can be captured from ambient air, offsetting emissions from distributed sources. In this paper, we show that CO_2 capture from air is physically and thermodynamically feasible, discuss the various routes available, and explain why NaOH solution is a viable sorbant for large-scale capture. An example system using NaOH spray is presented. With experimental data and a variety of numerical techniques, the mass trasfer of CO_2 to falling drops of NaOH solution is calculated, and an example contacting system developed. The cost and energy requirements of the contacting system are estimated and combined with estimates from industry and other research to estimate the cost of the complete system. We find that the cost of capturing CO_2 with the complete system would fall between 240 and 550 $/t-C, and improvements are suggested which could reduce the cost by about 100 $/t-C from the upper bound. Policy implications of this result are discussed.

1 Introduction

Global climate change is one of the most serious environmental problems we now face. In order to mitigate climate change, deep reductions in carbon dioxide (CO_2) emissions will be required in the coming decades. This necessity is at odds with fossil fuel's overwhelming dominance as an energy source. By capturing and storing CO_2 outside of the atmosphere, reductions in emissions can be achieved while fossil fuels and their associated infrastructure are phased out more slowly and thus at lower social cost. Given the extent of emissions reductions needed to stabilize atmospheric CO_2 concentrations and the inertia involved in shifting the world's primary energy sources, carbon capture and storage will likely constitute a substantial share of emissions reduction in the near- to medium-term.

Nearly all current research on carbon capture focuses on capturing CO_2 from large, stationary sources, such as power plants, as it is produced. Such plans usually entail capturing CO_2 from flue gas, compressing it, and transporting it via pipeline to a sequestration site, where it is injected under ground or otherwise stored. In contrast, systems described in this paper capture CO_2 directly from ambient air ("air capture"). The capture unit can be located at a favorable sequestration site, avoiding the need for a CO_2-transportation infrastructure. This strategy has the additional advantages that CO_2 emissions from any sector can be captured, including emissions from diffuse sources such as automobiles, and that the technology makes possible negative net emissions in the future.

2 Thermodynamic and physical limits of air capture

The proposition of air capture is fundamentally one of concentrating CO_2 – taking from it from a dilute state (360 ppm in the atmosphere) to a relatively pure gas ($> 90\%$ for compression to pressures required for underground sequestration). In the limit of a perfect mechanism for achieving this, we have only to overcome the free energy of mixing. It is given by $\Delta G = RT \ln(P/P_0)$, where in our case P is 1 atm and P_0 is 3.6×10^{-4} atm, for an energy requirement of 20 kJ/mol (1.7 GJ/t-C). This is quite modest compared with the energy liberated when burning fossil fuels, e.g. 650 kJ/mol-CO_2 (54 GJ/t-C) for gasoline (Agency, 2000).

Relative to other technologies for generating carbon-neutral energy, the land-use requirements for air capture are potentially very small. Dubey et al. (2002) compare the energy available in a square meter of land collected by biomass (0.003 kW) or from sunlight (0.2 kW), and the kinetic energy passing through 1 m^2 for windmills (0.6 kW) with the fossil energy that can be generated in producing the quantity of CO_2 passing through that square meter (100 kW). The conclusion is that land requirements for air capture coupled with fossil energy generation are potentially orders of magnitude smaller than for these other options.

Given that it is possible to extract CO_2 rapidly from the atmosphere in a relatively small area, we may be concerned that the process would be limited by local atmospheric transport of CO_2. Johnston et. al. (Johnston et al., 2003) have studied this problem with global atmospheric and chemical transport modeling. They conclude that the transport and circulation of CO_2 is such that the entire flow of anthropogenic CO_2 could be offset by a single global sink of no more than 75,000 km^2 in area, and with intelligent placement of sinks, a small fraction of that area would be needed. This is intuitively consistent with the observation that the atmosphere is relatively well-mixed with respect to CO_2. In general it seems that the issue of local CO_2 transport to a sink, and the related issue of depleted-CO_2 plumes that may be hazardous to plant life, can be easily resolved.

3 Routes to air capture

3.1 Organic carbon production

Many organisms naturally capture CO_2 through photosynthesis. One can effectively remove CO_2 from the atmosphere with land management and land-use changes which increase terrestrial biomass, such as growing a forest where there once was agricultural land. Estimates for the cost of these projects cover the range 0.1–28 \$/t-C (IPCC, 2000). Though even the high end of this range is small relative to other carbon management options, this strategy is fundamentally limited to one-time reductions. Once a plot of forest has reached maturity, it is no longer compensating for CO_2 emissions, since the CO_2 released as plant matter decomposes is in balance with the CO_2 absorbed as new plant matter forms.

Ocean flora has also been discussed as a means of carbon capture, the idea being that adding key nutrients to some parts of the ocean will generate large blooms of plankton which will take up carbon and draw it down to the deep ocean. Large scale experiments on this method have been conducted, so far with limited success (Buesseler et al., 2004; Buesseler and Boyd, 2003, for example).

Another means of capturing CO_2 with photosynthesis is to run a biomass-driven power plant with a carbon capture system. When the biomass is grown, it extracts CO_2 from the air which is later captured from the power plant flue gas with an amine system or other point-source capture system. This scheme is renewable, since each new crop of plants further extracts CO_2. Keith et al. (2004) have estimated the cost of CO_2 capture with this system at 160 \$/t-C.

3.2 Metal-carbonate production

For a chemical approach to air capture, some industrial waste streams are suitable for absorbing CO_2. In particular, steel slag and waste concrete, rich in calcium and magnesium oxides, readily react with CO_2 to form solid carbonates. Stolaroff et al. (2005) have analyzed a scheme for carbonating steel slag and waste concrete with CO_2 from ambient air, and estimate the cost as \$30/t-C. Many other researchers have studied concrete carbonation not necessarily associated with air capture (Fernandez et al., 2004). Iizuka et al. (2002), for instance, have estimated the cost at 32 \$/t-C[1].

Another approach is to add these kind of waste materials or suitable virgin materials such as limestone ($CaCO_3$) or soda ash (Na_2CO_3) to the surface layer of the ocean. The aim is to increase the alkalinity of the ocean, thereby increasing its capacity to uptake CO_2, indirectly decreasing atmospheric CO_2 concentrations (Kheshgi, 1995).

3.3 Capture with a regenerated sorbant

None of the above routes has the potential to capture a large fraction of anthropogenic CO_2 emissions; each has fundamental limitations on its scope. Biomass, for instance, is limited by the land available for cultivating biomass crops and by the secondary impacts of agriculture. The annual U.S. production of concrete and steel slag could capture less than 1% of U.S. emissions (Stolaroff et al., 2005). Ocean sequestration may be limited by available materials, area of suitable ocean surface, or problems associated with altering the ocean's chemistry.

To capture a large fraction of CO_2 emissions, all of emissions from the transportation sector (40% of total), for instance, it is natural to seek a sorbant which can capture CO_2 and then be regenerated and reused

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[1] Converted from 3300 JPY/t-C.

in a cycle. Most likely, this would be coupled with deep underground injection of CO_2, considered a viable method of large-scale, long-term CO_2 storage (Lackner, 2003).

The regeneration can be accomplished with a temperature swing, such as when amine solvents are heated, a pressure swing, such as a solid sorbant which releases CO_2 when exposed to a vacuum, or with a chemical reaction.

An ideal sorbant would have a binding energy with CO_2 just larger than the 20 kJ/mol required to pull it from the atmosphere, would be inexpensive, abundant, and non-hazardous. Research on new and novel sorbants with these characteristics is ongoing. However, two well-known sorbants which, while not optimal on the 1st condition, satisfy the latter three well, are aqueous solutions of calcium hydroxide ($Ca(OH)_2$) and sodium hydroxide (NaOH).

3.4 Metal hydroxide sorbants

A system using $Ca(OH)_2$ solution is outlined by Dubey et al. (2002). It consists of pools of water saturated with $Ca(OH)_2$ which absorb CO_2 as wind blows across the surface. Solid $CaCO_3$ is periodically collected from the bottom of the pool and Calcined (see Section 6.2.4). We consider this particular proposal kinetically unfavorable and prone to excessive water loss (see Section 5.2), but the principal is demonstrated. Dubey et. al. estimate a cost of about 80 \$/t-C for this scheme, but this figure has been criticized elsewhere (Herzog, 2003).

A related proposal is to use NaOH solution. $Ca(OH)_2$ is still used in the regeneration of the NaOH, and the end product – $CaCO_3$ to be calcined – is the same. However NaOH solution has the advantages over $Ca(OH)_2$ that it can have lower vapor pressure to prevent water loss, it can contain higher concentrations of carbonate for more efficient contacting systems, and is less prone to cause scaling problems in the contacting systems.

The NaOH approach is the primary subject of this paper, and an example system is presented in detail. The system follows on the authors' proposal in Keith et al. (2004) and is also discussed by Zeman and Lackner (2004). The latter gives a cost estimate of 25-75 \$/t-C, but does not give a specific description of the system. We consider this estimate incomplete.

4 Overview of example system

The example system proposed here uses an aqueous solution of sodium hydroxide (NaOH) to capture CO_2 from the air and then regenerates this solution. The appeal of this system is that the chemicals involved are all inexpensive, abundant, and relatively benign, and that the processes are all well-understood as current industrial-scale practices. It is a system which could be engineered with existing technology and which can scale to capture a significant fraction of CO_2 emissions without depleting scarce resources.

A top-level process diagram is presented in Figure 1. The numbers in each unit corresponds to the reaction from Table 1 occurring there. Table 1 summarizes the chemistry of the example system.

In the Contactor, the NaOH is brought into contact with atmospheric air and absorbs CO_2, forming sodium carbonate (Na_2CO_3). This carbonate-containing solution is then sent to the Causticizer. In the simpler formulation of the system (see Section 6.2), lime (CaO) is added to the solution so that Reactions 2 and 4 both occur in the Causticizer, in a series of stirred tank batch reactors. In an improved design (see Section 6.3), Reaction 4 is carried out separately in a unit called a Slaker. In either case, the Causticizer produces solid calcium carbonate ($CaCO_3$) and NaOH. The $CaCO_3$ is collected and sent to the Calciner

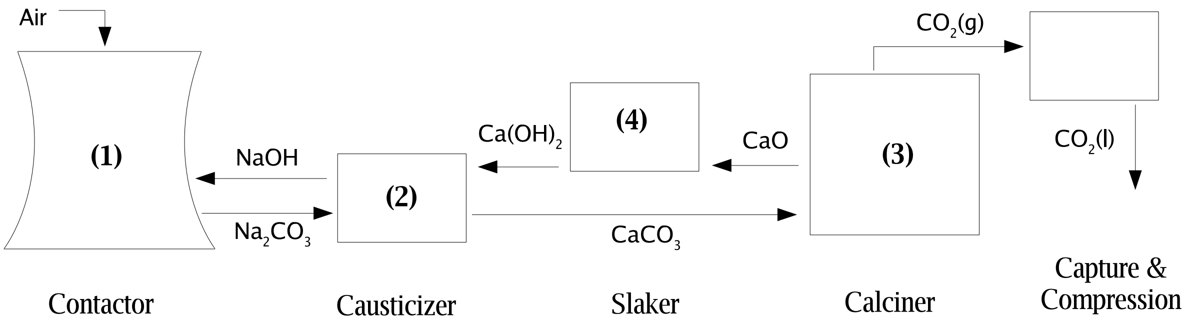

Figure 1: Top level process diagram of an example air capture system. Closed chemical loops of NaOH and CaO extract CO_2 from air convert it to a pure, compressed form for sequestration.

Table 1: Chemistry of example system

	Reaction			Enthalpy of reaction,[a] ΔH^O	
				kJ/mol-C	GJ/tC
(1)	$CO_2(g) + 2OH^-$	$\rightarrow$	$CO_3^{2-} + H_2O$	-110	-9
(2)	$CO_3^{2-} + Ca^{2+}$	$\rightarrow$	$CaCO_3(s)$	12	1
(3)	$CaCO_3(s)$	$\rightarrow$	$CaO(s) + CO_2(g)$	179	15
(4)	$CaO(s) + H_2O(l)$	$\rightarrow$	$Ca^{2+} + 2\,OH^-$	-82	-7

[a] Derived from Weast (2003).

while the NaOH is sent back to the Contactor. The Calciner heats the $CaCO_3$ until the CO_2 is driven off and CaO is re-formed. The CO_2 is collected and compressed for sequestration.

Whereas the other components all have counterparts in currently operating industries, the Contactor doesn't have an obvious analogy on which we can base cost and energy requirements. For the purposes of analysis, we will describe an example Contactor based on a power plant cooling tower. The next section discusses the issues associated with CO_2 extraction by NaOH and details the example unit.

5 Contacting with NaOH

CO_2 extraction from air with NaOH solution has been an established, well-known process for many decades (Greenwood and Pearce, 1953; Hoftyzer and van Krevelen, 1954). CO_2, even at ambient concentrations, is absorbed efficiently by solutions with high pH (Dubey et al., 2002). The most common industrial method of absorbing a gas into solution is to drip the solution through a tower filled with packing material while blowing the gas up through the tower. However, "packed tower" designs such as these are not ideal for processing a large amount of air with low removal efficiency[2].

An alternate strategy is to use an empty tower with the solution sprayed through, much like a power plant evaporative cooling tower or an SO_2-scrubbing tower for combustion flue gas. For the purposes of this paper, this strategy has the advantage that the costs are easier to estimate because of the simplicity of the

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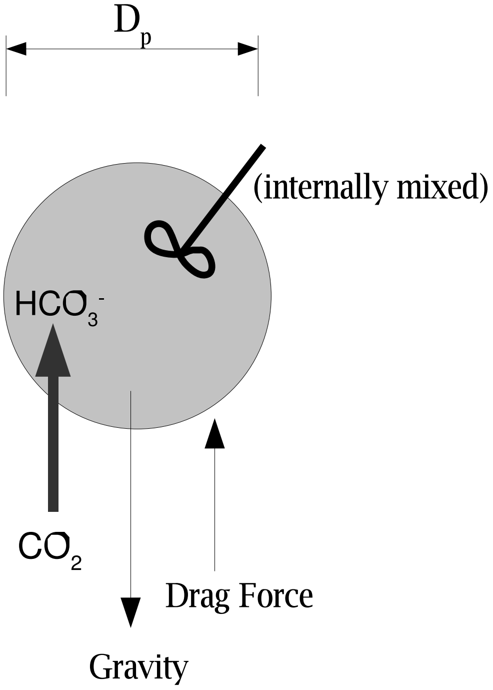
[2] Exponentially higher pumping energies are required for higher capture efficiencies of the CO_2 passing through the system. Because atmospheric air is so abundant there is no compelling reason to capture most of the CO_2 from any given parcel.

Figure 2: Diagram of numerical model of a falling drop of NaOH solution



design and the analogy to industrial cooling towers.

5.1 Mass transfer

The energy requirements for pumping and spraying NaOH solution depend on the rate of mass transfer of CO_2 from the gas to the aqueous phase; faster fluxes lead to less energy required per ton of carbon. To estimate the energy requirements of the example Contactor, we need to estimate the rate of CO_2 uptake by falling drops. Boundary layer theory is a useful tool for this application. A diagram of the model is shown in Figure 2.

While, in some experiments, controversy exists over whether air-side or liquid-side resistance is limiting for the absorption of CO_2 (Greenwood and Pearce, 1953; Hoftyzer and van Krevelen, 1954; Zeman and Lackner, 2004), we consider the low atmospheric concentration and the internal circulation of falling drops (Pruppacher and Klett, 1978) to indicate air-side resistance is dominant in our system (see Section A.2). This simplifies the problem and allows us to use empirical correlations for the mass transfer coefficient of falling drops from Bird et al. (1960). A detailed explanation of the mass flux calculation is given in Appendix A.

5.1.1 Model results

Figure 3 shows the predicted absorption of CO_2 by drops passing through our example Contactor, with assumptions consistent with Section 5.4. Integrating this curve over a typical drop size distribution produced by a spray nozzle (see Figure 14), gives an average absorption of 0.4 M. Considering how far the solution must be lifted (120 m), this amounts to a theoretical pumping energy requirement of 6.2 kJ/mol or 0.51 GJ/t-C, which is quite small.

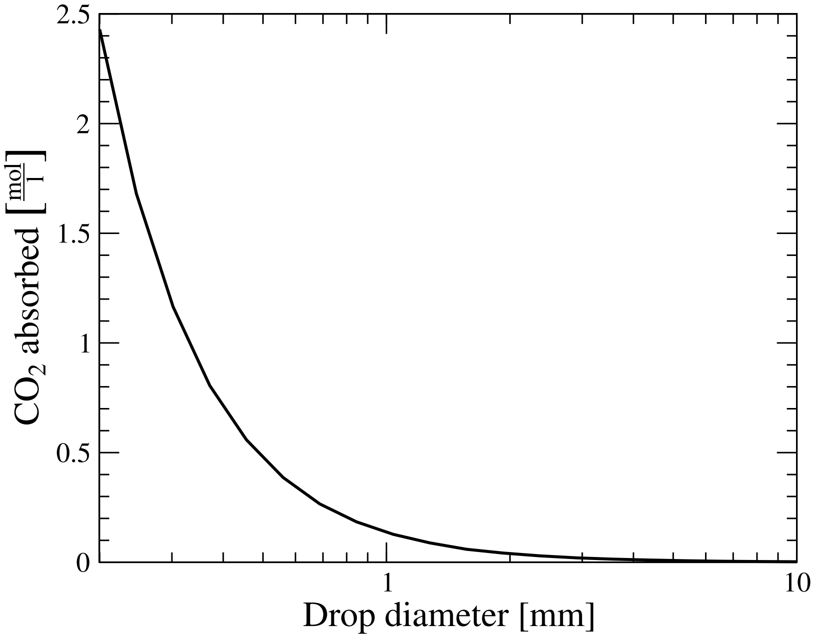


Figure 3: CO_2 absorbed by drops falling through a 120 m Contacting tower

5.1.2 Experimental procedure

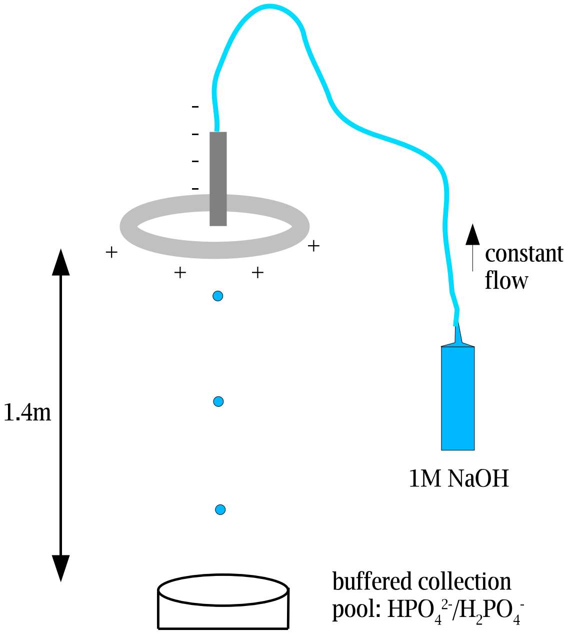
In order to verify the results obtained from the mass-transfer model, an empirical measure of CO_2 absorption was devised. The experimental apparatus is depicted in Figure 4. A slow, steady flow of 1M NaOH solution is pumped through a small (0.5 mm inner diameter), electrically-grounded metal tube. Below the end of the tube, a metal ring charged to $\sim +1.5$ kV creates an electrostatic field which pulls small drops from the tip of the tube (much smaller drops than would be possible by gravity), which fall through a known distance of atmospheric air into a collection dish. The collection dish initially contains 10 ml of 0.5M potassium phosphate buffer (KH_2PO_4/K_2HPO_4, $p\mathrm{H} \approx 7.2$) which keeps the pH of the collected sample low enough that additional CO_2 is not significantly absorbed after the drops have fallen.

The frequency of the drops leaving the tube is recorded manually, and this is used to calculate the average drop diameter. After 0.1–1.5 ml of sample is collected, the Na^+ concentration in the collected sample is measured with an Ion-Selective Electrode. The sodium acts as a tracer for the volume of drops collected. The carbonate concentration in the collected sample is measured with a Total Carbon Analyzer. The sample carbonate concentration is compared with a control sample collected directly below the tube.

5.1.3 Experimental results

The measurements of CO_2 uptake are compared with the corresponding model prediction in Figure 5. Essentially, the numerical model and the experimental data agree within a factor of 2, a difference which could reasonably be explained by imprecision in the model or bias in the experimental method. It could also indicate that the assumption of air-side limitation to mass transfer is not appropriate, and that some degree of water-side limitation is slowing the mass transfer. Even if this is the case, and, for instance, twice the pumping energy is required as that assumed in the cost calculations, the overall cost of the example system

Figure 4: Experimental apparatus for measuring CO_2 uptake of falling drops of NaOH solution



is not substantially affected by this change. As long as the system can be made to capture carbon on the order of 0.1 M per pass or more, the pumping costs of the contactor are tenable.

5.2 Water loss

We would expect any aqueous-based contacting system to be subject to evaporative water loss. The low concentration of CO_2 in the atmosphere makes this especially important, since relatively more contact between gas and liquid phases is required per unit of CO_2 captured.

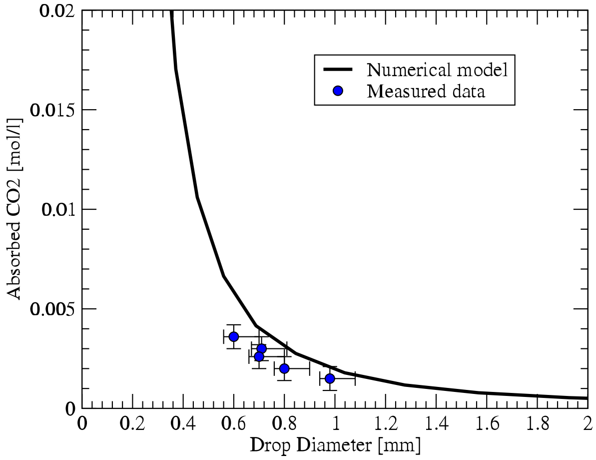
Again we turn to boundary layer theory and the assumption that air-side resistance is limiting. Appendix B gives a detailed explanation of the calculation of water loss. At the heart of the issue we have the relationship:

$$\frac{\dot{M}_{H_2O}}{\dot{M}_{CO_2}} = 1.5\frac{C_{H_2O} - C_{H_2O,vap}}{C_{CO_2}} \tag{1}$$

This essentially states that the ratio of the mass of water lost to the mass of CO_2 captured is proportional to the difference between the fluid vapor pressure and the ambient water concentration (humidity). For a zeroth-order estimate of water loss, we can consider this ratio for a dilute solution and typical ambient conditions. At 20^{o}C and 60% relative humidity, this comes to 38 mol-H_2O/mol-CO_2, or 58 m^3-H2O/t-C, which is very large indeed. Complexities arise, however, since the evaporating water cools the liquid and lowers the vapor pressure. This value represents the limit where air and water temperatures do not change significantly, such as transfer at the surface of a lake or large pool.

Accounting for temperature and other effects (see Section B.2), we find the water loss in an arid Climate to be about 10 m^3-H2O/t-C. At municipal water prices, this would add $\sim$ 30 \$/t-C to make up. And if air capture were used on a large scale, it could demand billions of cubic meters per year of water in the U.S. – on the order of total consumptive use for power plant cooling.

Figure 5: Absorbed CO_2 of drops falling 1.4 m – comparing theory with measured



Another complexity arises in that the vapor pressure of NaOH solutions is lower than for pure water. Solutions of high enough concentration even become hydroscopic, absorbing water from the air. In theory it is possible to adjust the initial NaOH concentration in a contacting system for zero net water loss based on ambient conditions. In fact, the point of zero net loss is a stable equilibrium if the working solution is in a closed loop. However it is certainly possible that demands of the Causticizer or other practical concerns will require the system to run with significant net water loss. Siting the system near an inexpensive water source or in a location with favorable climatic condition would then become an important consideration. For the purposes of the cost estimates in this paper, procurement of water was not accounted for.

5.3 Solids formation

At higher carbonate concentrations, solids formation may become an issue. Calculations with the chemical equilibria modeling software Chess were performed. The results are displayed in Figure 6. It predicts solids formation with carbonate concentrations larger than about 0.4 M in a solution with an initial NaOH concentration of 5 M. However, the solids formation may be kinetically limited, and in any case it may not be a practical concern for the system with its open-tower design. It would be more troublesome for packed-tower Contactors which would also likely be aiming for higher solution carbonate concentrations.

5.4 Example Contactor

With consideration of the findings discussed above, we have developed an example Contactor: an open tower, 120 m high and 100 m in diameter, where NaOH solution is sprayed from the top and air is blown

Figure 6: Equilibrium speciation of carbonates added to a 5M NaOH Solution

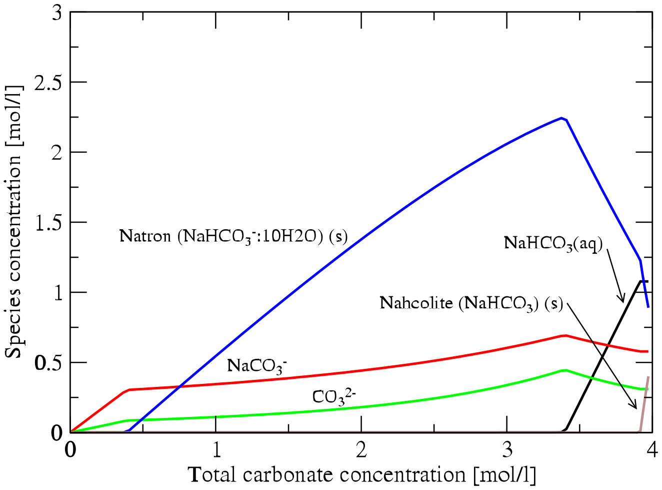
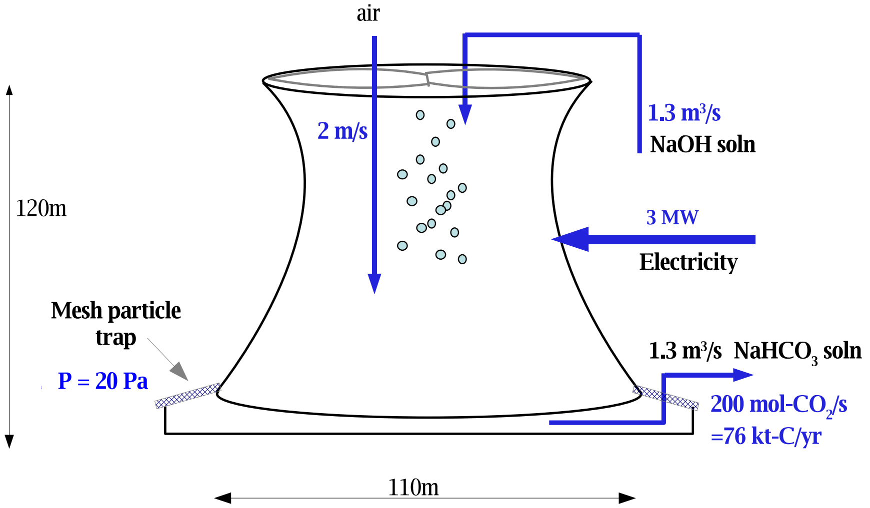


Figure 7: Example Contactor with key input/output flows



down through it co-currently[3] A cooling tower of equal dimensions can be built today for about US$8 million which includes mechanisms for spraying and collecting liquid. The major difference in our design is the addition of fans to force air through co-currently. More sophisticated infrastructure for handling and moving the working solution may also be required. For the cost presented in Section 6, we assume that these additions increase the capital cost of the tower by no more than 50%, to US$12 million. Additionally, operation and maintenance (excluding energy use) was assumed to be 5% of capital cost per year.

6 Cost Estimates

6.1 Lower bound

Theoretically, the energy demand of the proposed system is dominated by the Calciner, where $CaCO_3$ is heated to release the captured CO_2, Reaction 3. (As discussed later in Section 6.2.6, this dominance is borne out by cost estimates of the components of the total system.) This reaction has a large thermodynamic energy requirement which must be overcome in even the most advanced calcining system. We set the lower-bound cost from the current cost of industrial calcination.

The calcining operation in its simplest form is performed by the lime manufacturing industry at large scale and using long-established technology. In the production of high-calcium quicklime (CaO) in particular, crushed Calcite ($CaCO_3$) is heated in a kiln to form the product. Through the industry's long experience, it has developed a very efficient process, with energy requirements close to the thermodynamic limit (17 GJ/t-C, compared with the limit of 15, is typical). One can make arguments for how the costs of the other components of the air capture system can be greatly reduced by advances in design or economies of scale, but it is unlikely that a calcination-based air capture system could be less expensive than the current industrial calcining process, which has been optimized through decades of industrial experience[4].

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[3] While countercurrent designs are more typical for air/liquid contacting, we found that a co-current design does not drastically diminish the contacting efficiency and it prevents small drops from being lost by entrainment from the top of the tower.

[4] A possibility which might be argued as a way to reduce the energy requirements below the requirement of Reaction 4 (and of

The market price of high-calcium quicklime should reflect the industrial cost of calcination, inclusive of operation and capital recovery. One major adjustment is needed, however, because this price will include the cost of the raw material – crushed limestone. This is not needed in the air capture system, aside from a small amount of make-up lime, since the material is reused. Miller (2003) reports that the average price of this product in the United States is 285 \$/t-C (converted to C terms). Subtracting the average price of crushed limestone sold for lime manufacturing of 44 \$/t-C (Tepordei, 2002), this gives 240 \$/t-C.

6.2 Upper bound

6.2.1 Overview

To give an upper bound to the cost of air capture, we will present a system assembled, as much as possible, from off-the-shelf components with what are meant to be conservative assumptions about the cost of any modifications. We use the example Contactor discussed in Section 5.4.

A more complete analogy than the lime manufacturing industry is offered by the pulp and paper industry, with what is known as the Kraft Process. It is essentially the same system as the one proposed for air capture, taking Na_2CO_3 solution and regenerating it to NaOH by means of CaO and a calcination loop. The main differences are that the NaOH is being carbonated by air instead of in a wood pulping reaction and that we wish to capture CO_2 emitted from the Caliner. These and other minor differences between the Kraft process and the proposed system are discussed below. Each component from Figure 1 is discussed in turn, except that the Slaker is combined with the Causticizer.

6.2.2 Contactor

As a basis for cost and energy estimates, we use the example Contactor presented in section 5.4. Additional parameters, where needed, were selected to be reasonable but not optimized, and therefore conservative with respect to their influence on unit cost. The drop size distribution was taken from a typical hollow-cone spray nozzle (Fair and et al, 2001) with a volume-mean diameter of 0.7 mm. This is probably not the optimal distribution – smaller drops would be more efficient – but it is selected for being well-known as easy to achieve.

A velocity of 2 m/s was selected for the rate that fans blow air through the tower. The air velocity trades off higher CO_2 throughput, i.e. lower capital cost, with increased fan energy (since fan energy goes as the square of velocity). While this value is not optimized, it falls in the likely range of the optimal value since capital costs balloon for air speeds much below this, and fan electricity costs dominate for values much above this.

The capture efficiency trades off higher CO_2 throughput, i.e. lower capital cost, with increased solution pumping. Because higher efficiencies require exponentially more energy to achieve, but low efficiencies drive up capital costs, the chosen value 50% is in the reasonable range.

Finally, the initial NaOH concentration is adjusted in the range 3–6 M to minimize water loss based on local conditions. The hydroxide concentration is thus well in excess of the predicted concentration of carbonate captured in each pass of the solution, 0.2 M.

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industrial calcination) is to construct a system which captures the energy from Reaction 3 for heat or useful work, something which cannot be accomplished in quicklime manufacturing. This appears quite possible, but the captured energy would likely be used for several purposes which aren't part of quicklime manufacturing: solvent regeneration (or oxygen production in an oxyfuel system), dewatering and drying of $CaCO_3$ mud, and electricity for pumps and fans.

6.2.3 Causticizer

In this step, the Na_2CO_3 solution from the capture unit is mixed with CaO from the Calciner. Reactions 2 and 4 occur in one or more gently-stirred batch reactors. A near-perfect analogy can be drawn between this and the causticizing step in the Kraft recovery process used in the pulp and paper industry. The Kraft process takes spent pulping chemicals, primarily Na_2CO_3 and Na_2S, and regenerates them to NaOH and Na_2S with the same chemical reactions as above. The substantive differences between the Kraft process and the proposed Causticizing process for air capture are as follows.

Sulfur content The presence of sulfide aids the preparation of wood pulp, and so must be carried through the Kraft recovery process. The process has been tested, however, without the addition of Na_2S, and the primary result is an improvement in the conversion efficiency of Na_2CO_3 to NaOH by a few percent, and in general the sulfur only complicates the process. Since our proposed system does not require any sulfide, we expect it to run a few percent more efficiently than the Kraft equivalent.

Temperature In the Kraft process, the slaking and causticizing steps are typically performed with a solution temperature in the range of 70-100^{o}C. However, the solution entering this step in the proposed system will be at ambient temperature or cooler. The solution is heated by the slaking reaction; assuming a (typical) concentration of about 2 mol/l CaO added, the slaking reaction will increase the solution temperature by about 20C^o, but that would only bring the solution to, perhaps, 40^{o}C. While the equilibrium conversion efficiency of Na_2CO_3 to NaOH is higher at lower temperatures, the kinetics become prohibitively slow. Without changing the process design to accommodate significantly longer residence times, we will have to add additional heat to the solution. Another 30C^o would bring us into the industrial range. We can do so with a liquid-to-liquid heat exchanger and a low grade heat input of (assuming the exchanger is 80% efficient) 14 kJ/mol-CO_2, or about 1 GJ/ton-C.

Solids content In the Kraft process, the initial Na_2CO_3 solution contains organic particles and insoluble minerals (“dregs”) in the part-per-thousand range. The dregs impair the performance of the process and so most must be removed in a clarifier. For the proposed system, the entire dreg-removal subsystem can probably be eliminated. The source of contamination most analogous to the dregs in the proposed system is fine particles captured from the air along with the CO_2. Assuming a particle concentration of 100 μg/m^3 and equal absorption efficiency with CO_2, the particle concentration in solution will be in the range of 10 parts per million.

Given the small and favorable differences between the Kraft process and our adaptation of it, a conservative estimate of the monetary and energy costs of running this component can be lifted directly from the pulp and paper industry.

6.2.4 Calciner

Calcination is the process where $CaCO_3$ is heated above 1000^{o}C to make CaO. The calciner in our example system is a close analogy with that paper industry since it is also starting with $CaCO_3$ mud produced during causticizing. It is possible to remove more of the water in the $CaCO_3$ mud before calcination. The pulp and paper industry has presumably optimized the trade-off between capital expenditure and mechanical energy for dewatering and energy cost for calcining for their circumstances. However, with the higher energy costs we have assumed a more energy-efficient design would be optimal. Thus, on this parameter, it is conservative to assume the same water content as in paper mill calciners.

6.2.5 Capture and compression

In contrast to current industrial systems, the air capture system must, of course, capture CO_2 from the calciner. The most straightforward method for doing this is to use an amine-based CO_2 capture system. The CO_2 concentration in the exhaust gases would approach 20% (dry basis), slightly lowering the capital and energy costs of amine capture compared to existing estimates for capture from coal-fired power plants (14% CO_2). Furthermore the water in the lime mud becomes high-temperature steam in the calciner. This steam can be used as a heat source for regeneration of the amines. Of the 32 GJ/t-C of low-grade heat available from a typical fluidized bed calciner (Adams, 1989), roughly 14 GJ/t-C are required for amine regeneration.

The cost and energy requirements of the Amine system are based on the model developed for Rao and Rubin (2002), with appropriate modifications (Rao, 2004), which includes all direct and indirect capital costs, maintenance, and energy. The amine system captures both CO_2 from the calcination reaction and CO_2 from combustion of the fuel, which is assumed to be either natural gas or gasified coal. Thus for every unit of CO_2 captured from air, about 1.5 units must be sequestered.

6.2.6 Results

The estimated cost of (net) carbon capture for the system as described is 550 \$/t-C. This cost presented in Figure 8, broken into major components. The required heat input is 50 GJ/t-C[5] (see Figure 9 for component contributions), which, for simplicity, is assumed to come from natural gas or gasified coal. Depending on fuels used and the source of electricity, the system is burning and sequestering 0.5–1.5 extra tons of carbon for every ton captured from the air.

The estimate uses the price and energy requirements of a “turnkey” causticizing and calcining system for the pulp and paper industry (Flanagan, 2004), the amine model, and the example Contactor discussed above. Some additional assumptions were required. A capital charge rate of 15% (equivalent to a 20 year plant life and 14% discount rate) was used. Fuel was priced at 4 \$/GJ, and carbon-neutral electricity was priced at 0.07 \$/kW-hr. When not available, operating and maintenance costs were assumed to be 5% of capital per year.

6.3 An improved system

This section describes some potential improvements to the upper bound design which may offer substantial energy savings. The major improvements are that (1) the calciner is fired in oxygen, so that the exhaust gas can be directly compressed without the need for an amine system, and (2) the slaking reaction, Reaction 4, takes place in steam at higher temperature and pressure, making the energy of this reaction available for higher-grade applications. There are also some minor changes to the Contactor – a more aggressive assumption about drop size (mean diameter$\approx$ 0.5 mm), and faster air flow rate (4 m/s). Other parameters and assumptions about energy price, discount rate, et cetera, will be consistent with Section 6.2.

The cost and operating parameters of the oxygen plant follow Dillon et al. (2004). Assuming the same specific heat requirements and fuel as in the previous section, a little over 1 mole of O_2 is needed for each

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[5] Assuming a conversion efficiency of thermal to electric energy of 50%. Electricity could come from a non-thermal, carbon-neutral source.

Figure 8: Estimated costs per net ton of carbon captured of example systems

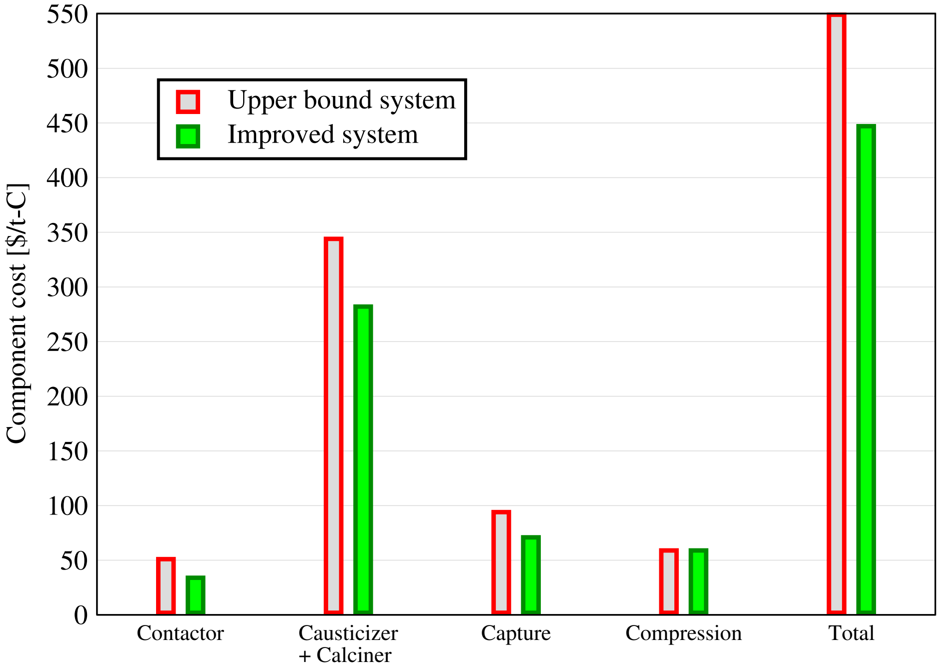
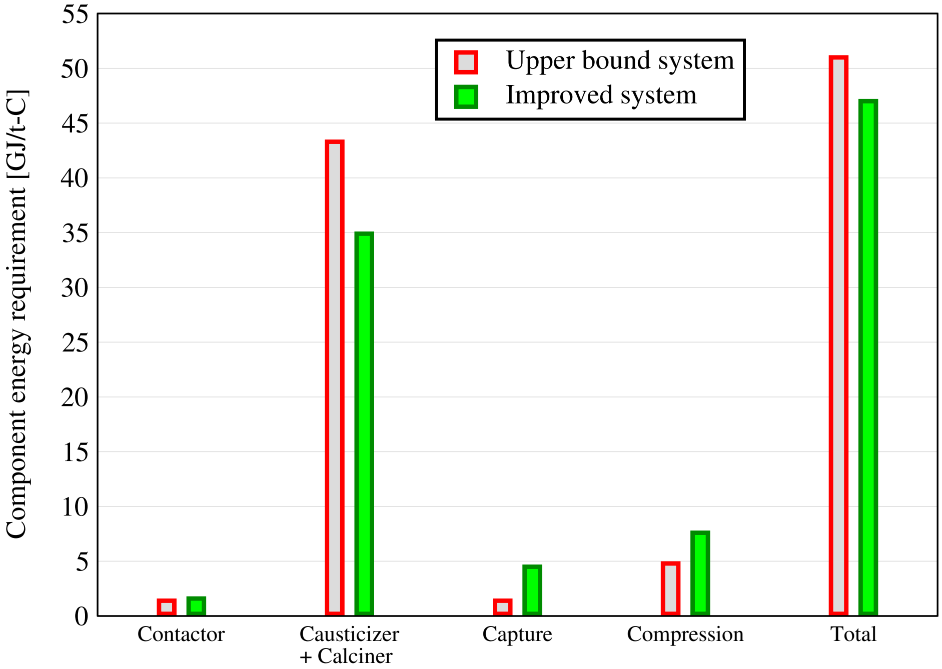


Figure 9: Estimated energy requirements per net ton of carbon captured of example systems



mole of CO_2 captured. Using the oxyfuel system, the cost of capture is reduced from 94 for amines to 67 $/t-C, though admittedly, this ignores important structural differences between the oxygen and air-fired calciners that would affect the cost.

It is theoretically possible to carry out Reaction 4 in steam, at higher temperature, e.g. 600^oC. If this could be practically achieved, significant energy savings would result. If this reaction drove a turbine to generate electricity at 30% efficiency, 2.7 GJ/t-C would be saved (58 $/t-C under our assumptions).

Finally, there is no obvious reason why the Contactor could not operated with smaller drops, in which case it would be beneficial to increase the air flow rate and save on capital costs. Making these modest adjustments brings the cost of contacting down to 34 $/t-C from 51.

Together these improvements give an estimated cost of 450 $/t-C and 46 GJ/t-C (see Figures 8 and 9), though this is an incomplete estimate since there will be differences in capital costs and energy efficiency in an improved system. In particular, there is significant room for improvement in dewatering and heat integration. If the water content of the mud could be decreased by a factor of two, holding all else constant, there would be an energy savings of 7 GJ/t-C (44 $/t-C, in our model). There is also opportunity for economies of scale to substantially reduce costs. The capacity of a typical pulp and paper calciner is an order of magnitude smaller than that of the example Contactor, which in turn has a carbon throughput about one tenth of a 1000 MW coal power plant, for example. The larger analogues could be more efficient in capital and energy.

7 Capture cost in context

The estimated cost of air capture of 240–550 $/t-C is much more than current and likely near-term carbon taxes in the U.S.. Under the Kyoto Protocol, for instance, the carbon price would have been 53 $/t-C by 2010. The recently proposed McCain-Lieberman bill called for a carbon price between 33 and 58 $/t-C (Economist, 2004). The Nation Commission on Energy Policy report calls for a price of 26 $/t-C (on Energy Policy, 2004).

This cost is also significantly more than the capture cost from point sources. For instance, the cost of CO_2 capture from power plants with an Amine system is expected to be in the range of 160–260 $/t-C(Rao and Rubin, 2002).

Compared with other means of reducing carbon emissions from the transportation sector, however, the cost of air capture could be substantially smaller. The cost of removing carbon by switching to Hydrogen powered vehicles has been estimated at 1000 $/t-C. A rough estimate based on current research modeling large scale ethanol production for the cost of emissions avoidance by switching to ethanol is 500–1300 $/t-C (Morrow, 2004).

8 Conclusions and Discussion

In this paper, we discussed the various routes available to capture CO_2 from ambient air, and argue that a large scale endeavor would require a regenerated sorbant. We explain why NaOH solution is a viable sorbant, and present an example system for capturing and compressing CO_2 using NaOH and CaO. We argue that the cost of capturing CO_2 with the example system (or any regenerated alkali-metal sorbant) is not likely to be lower than 240 $/t-C or significantly higher than 550 $/t-C, and improvements are suggested which could reduce the cost by about 100 $/t-C from the upper bound.

We note that there is no fundamental physical limitation on inexpensive, large scale carbon capture from air. Indeed, advances in technology may make the process significantly less costly than our lower bound by using a novel sorbant. Even if no such advances are made, however, the availability of air capture at the estimated cost still has important implications.

The example system described here is not likely to be useful for capturing carbon from point sources such as power plants, since capture at the source is much less costly than the estimates given here. If viewed as a means of reducing carbon from the transportation sector, air capture may be less costly than the alternatives, especially as a transitional strategy (CO_2 from existing fossil-fueled vehicles is captured while carbon-neutral vehicles are phased in). The cost of \$550/t-C is equivalent to \$1.35 per gallon of gasoline, which is smaller than the tax in many European countries. However, along with the cost requirements of air capture, the substantial energy demand should be considered. The large energy requirements of the system would be filled with increased use of fossil fuel. For carbon-neutral gasoline vehicle, 1.5–2.5 times as much carbon must be extracted, processed, and handled as for that vehicle operating without capture. And even the lower bound, which comes to \$0.59 per gallon, is substantial compared with the cost of efficiency improvements, many of which are available at negative cost. It is obvious that an air capture scheme should not be pursued without having exhausted these.

In a broader sense, the cost of air capture sets an upper bound on the cost of greenhouse gas mitigation in general. Since this scheme can offset emissions from any sector with equal ease, no greenhouse gas mitigation strategy should ever be pursued which is more expensive than 550 \$/t-C. This cap on the cost of mitigation is an important consideration for policy makers developing a regulatory framework.

Another important feature of air capture is that makes possible negative net greenhouse gas emissions. While the scenario of negative net emissions will not likely occur for at least several decades, if at all, it constitutes an option (in the economic sense) which hedges against the possibility of more severe climate sensitivity. The existence of this option at 240–550 \$/t-C influences the optimal choice of climate policy today (Keith et al., 2004). With this option we should shift more of our emissions reductions to the future than we would in its absence.

Though the example system given here can be built with current technology, any air capture system is not likely to be used for several decades, once reductions through efficiency and capture at point sources have been made. In the mean time, research on systems like the example, in particular a pilot-scale demonstration, would make the above conclusions more forceful. Long-term research into more advanced, less energy-intensive systems is also recommended.

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A Mass transfer modeling

This section details the process of calculating the CO_2 absorption of falling drops as discussed in Section B.1

A.1 Dynamics of falling drops

The force balance in the vertical direction for a falling drop gives:

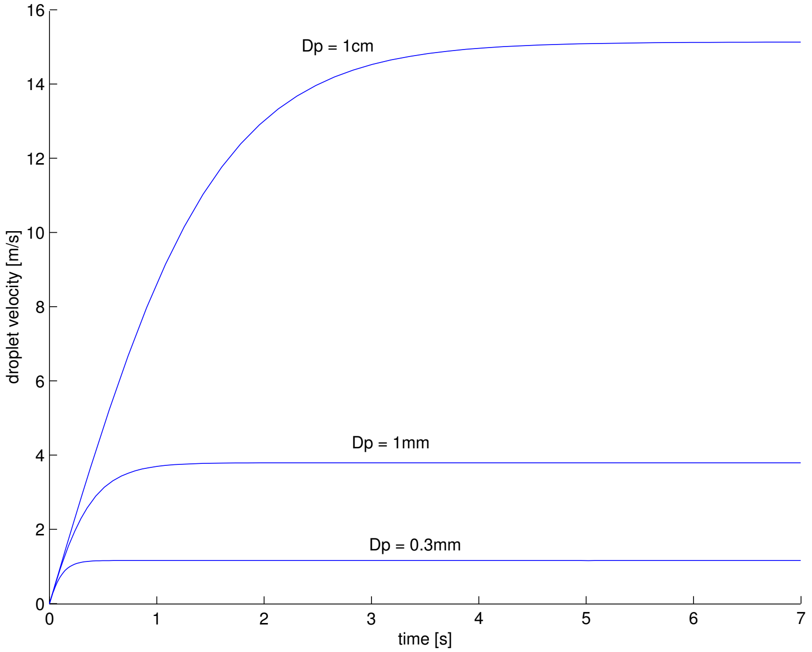
$$\frac{dv}{dt} = g - \frac{\pi C_D \rho D_p^2 v^2}{8 m_p} \tag{2}$$

where C_D is an implicit function of D_p and v by empirical relation to Re (Seinfeld and Pandis, 1998). Integrating numerically gives the results shown in Figure 10.

The drop approaches a terminal velocity which depends on the drop size. This is given by the steady-state simplification of Equation 2:

$$v_t = \left(\frac{4 g D_p \rho_p}{3 C_D \rho} \right)^{1/2}$$

Figure 10: Velocity of a falling droplet as a function of time



This implicit function can be used to calculate v_t as a function of particle size numerically. The results are shown in Figure 11.

Integrating Equation 2 twice allows us to find the contact time with air of a drop of a given size falling a given distance. The results for a $10\,m$ drop are shown in Figure 12.

A.2 Flux to falling drops

The characteristic timescale for aqueous-phase diffusion, τ_d is:

$$\tau_d = \frac{R_p^2}{\pi^2 D_{aq}}$$

when internal mixing is negligible (Seinfeld and Pandis, 1998). This amounts to about 13 s for a $1\,mm$ drop – fairly slow. However, for falling drops with $D_p > 200\ \mu m$, internal circulation develops (Pruppacher and Klett, 1978), then the timescale is on the order of:

$$\tau_d = \frac{R_p \mu_l}{v_t \mu_{air}}$$

which is small compared with contact times for falling drops; for a $1\,mm$ diameter droplet, $\tau_d = 0.006\ s$. So we assume that mass transfer to drops larger than 200 μm is limited by gas-phase diffusion.

Flux through the gas phase for falling drops is given by,

$$J_A = k_c(c_{\text{inf}} - c_s) \tag{3}$$

Figure 11: Terminal velocity of falling droplets

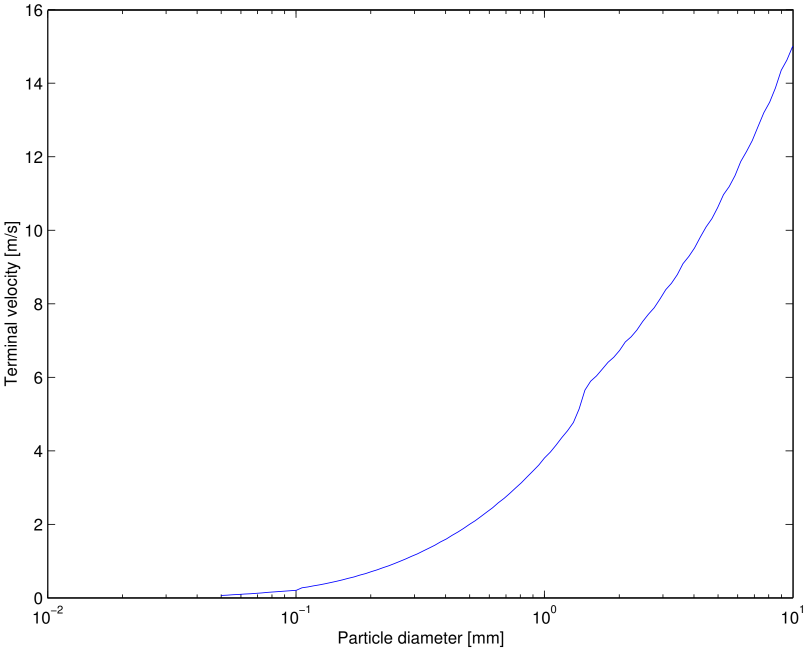
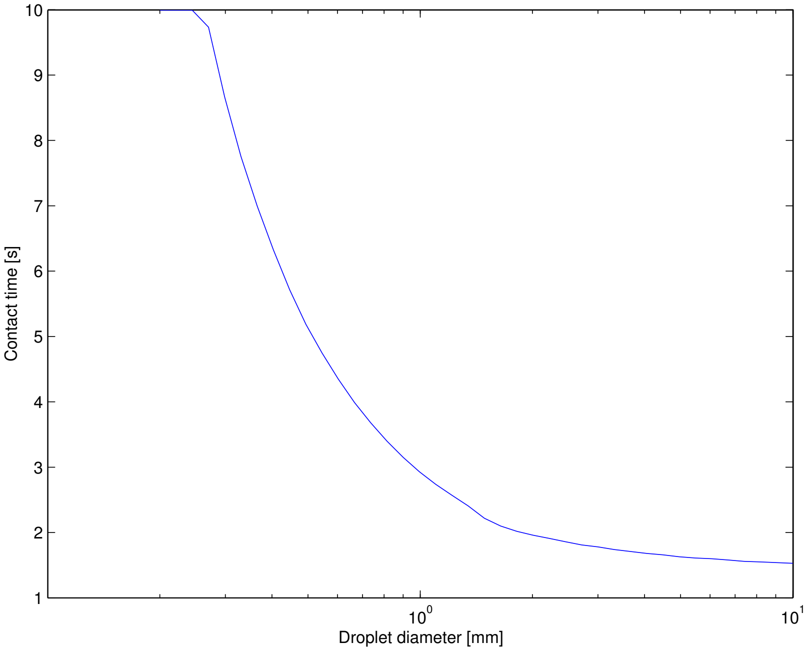


Figure 12: Contact time for drops falling through $10\,m$ of air



where c_s is the concentration of CO_2 in equilibrium with the surface concentration. We assume this to be zero, which is a good approximation for well-mixed solutions with $pH > 10$. k_c can be estimated by

$$Sh = \frac{k_c D_p}{D_g}$$

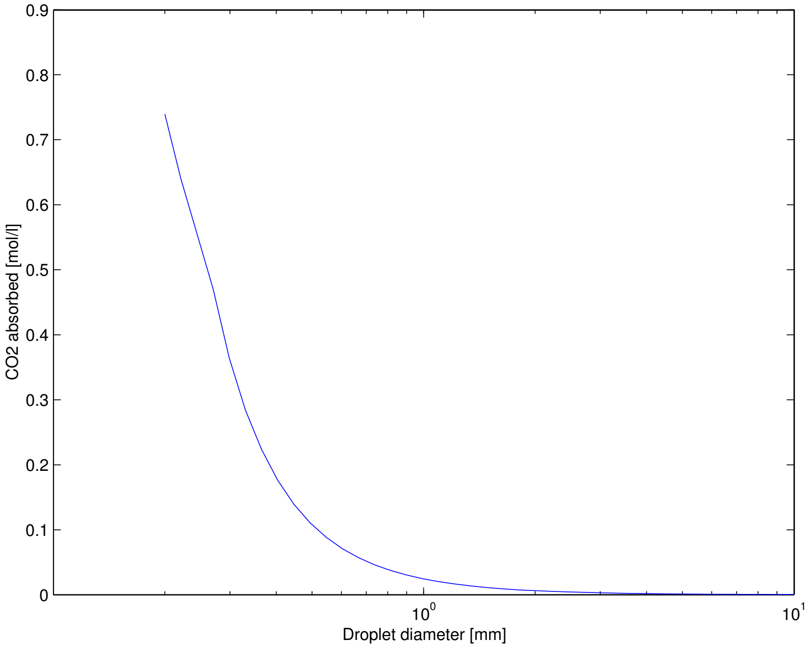
and the empirical relation

$$Sh = 2 + 0.6 Re^{1/2} Sc^{1/3}$$

for falling drops (Bird et al., 1960).

By integrating Equation 3 over velocity profiles as in Figure 10 with limits given by Figure 12, we can estimate the total mass of CO_2 absorbed into a drop over a free fall of $10\,m$ through atmospheric air. The results are shown in Figure 13.

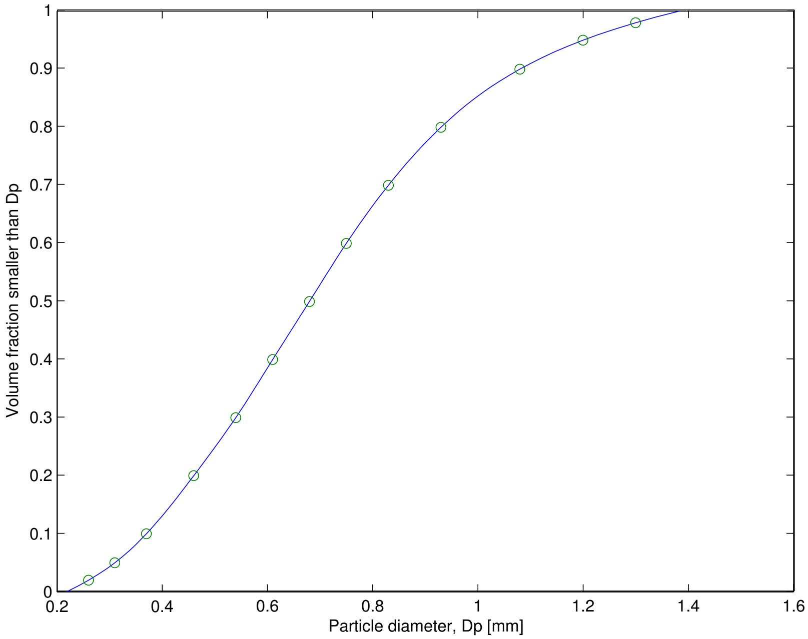
Figure 13: CO_2 absorbed by drops falling through $10\,m$ of air



The limits of the numerical integration can be adjusted for different fall distances, and the drag force conditions can be adjusted for moving air. To match the conditions of the example tower, we'll use a height of 120 m, and a co-current air flow of 2 m/s. In the reactor situation, drops are not always exposed to atmospheric concentrations of CO_2, since the CO_2 is depleted as it passes through the tower. Assuming an outlet CO_2 concentration of 50% of ambient, and a log-linear concentration gradient through the tower, the average air concentration is $0.72 \times 370 = 266$ ppm.

Dispersion systems produce a distribution of drop sizes. The distribution for a typical hollow-cone spray system producing volume-mean-diameter drops of $0.7\,mm$ is shown in Figure 14 (adapted from Fair and et al (2001)). The mean diameter can be adjusted by choice of spray nozzle and liquid pressure. In this distribution, about 2% of drops have a settling velocity smaller than 1 $\frac{m}{s}$, and are predicted to absorb CO_2 up to the chemical limit. Since the absorption mechanism of these small drops is not easily modeled, the maximum carbonate is conservatively capped at 2 M. About 10% of the drops are larger than $1\,mm$, and thus don't absorb CO_2 efficiently.

Figure 14: Typical cumulative volume distribution of drop sizes (Fair and et al, 2001)



In addition to the work required to lift the solution, energy is required to generate the small drops. There are many systems for dispersing liquids in air, utilizing different mechanisms of breakup and varying widely in energy requirements. Flat-spray and hollow-cone nozzles are common, relatively low-energy-cost solutions (Fair and et al, 2001). A pressure drop must be maintained across the nozzle in order to effect the breakup. A survey of spray nozzle manufacturer's specifications (Allspray, 2002) indicates that, having chosen an appropriate nozzle, 0.5–$1\,mm$ drops can be readily generated with a $10\,psi$ pressure drop. This amounts to about $7\,m$ of water head. This is included in the cost and energy calculations for the example Contactor.

B Evaporative water loss modeling

B.1 Mass Transfer

Whatever the shape and nature of the contacting unit, we assume that the solution is a sufficiently good absorber (e.g. a strong caustic solution) that mass transfer of CO_2 is limited by diffusion through the air boundary layer. This contactor must have transmissivity through the air layer, denoted k_{g,CO_2} and some interfacial area, a. The rate of mass transfer of CO_2 from the gas to liquid phase for any differential piece of the Contactor is then given by

$$\dot{M}_{CO_2} = k_{g,CO_2}\, a\, (C_{CO_2,bulk} - C_{CO_2,interface}) \tag{4}$$

and we approximate $C_{CO_2,interface} = 0$, which is appropriate for quickly-reacting solutions, such as NaOH.

The evaporation of water can also be considered an air-side limited diffusion process with the same interfacial characteristics as for the CO_2 transfer. In analogy with Equation 4, the mass-transfer rate is given by

$$\dot{M}_{H_2O} = k_{g,H_2O}\, a\, (C_{H_2O,bulk} - C_{H_2O,interface}) \tag{5}$$

where $C_{H_2O,interface}$ is the vapor pressure of water at the interface.

Boundary layer theory predicts that k_g is directly proportional to the diffusivity, D of the compound. Thus k_g for various compounds can be related by

$$\frac{k_{g,A}}{D_A} = \frac{k_{g,B}}{D_B}$$

which implies that

$$\frac{k_{g,H_2O}}{k_{g,CO_2}} = \frac{D_{H_2O}}{D_{CO_2}} = 1.5 \tag{6}$$

at 20^oC.

Taking the ratio of Equations 5 and 4 yields a differential relationship between the mass of CO_2 and H_2O transferred:

$$\begin{aligned}\frac{\dot{M}_{H_2O}}{\dot{M}_{CO_2}} &= \frac{\frac{dC_{CO2}}{dt}}{\frac{dC_{H2O}}{dt}} = \frac{dC_{H_2O}}{dC_{CO_2}} \\ &= \frac{k_{g,H_2O}\, a\, (C_{H_2O} - C_{H_2O,vap})}{k_{g,CO_2}\, a\, C_{CO_2}} \\ &= 1.5\frac{C_{H_2O} - C_{H_2O,vap}}{C_{CO_2}}\end{aligned} \tag{7}$$

where C_{H_2O} and C_{CO_2} are measured in the bulk air. $C_{H_2O,vap}$ is in general a function of the temperature and composition of the fluid, and thus will change as CO_2 is absorbed and water evaporates.

B.2 Temperature variation

By extending boundary layer theory to heat transfer, and using a few simplifying assumptions, we can come up with an estimate of the change in temperature of the working fluid as a function of CO_2 captured. We assume that resistance to heat transfer from the bulk air to the working fluid is dominated by the air-side boundary layer. The bulk air is considered to be well-mixed with respect to temperature, and the heat flow at any given stage in the reactor has reached steady state.

A complete energy balance on the working fluid includes many terms. There is heat lost from the vaporization of water, heat gained from $NaHCO_3$ formation, conduction from the air, conduction from the contactor surfaces, and frictional and viscous heating. These latter two effects will be ignored; contactor surfaces are considered to have equilibrated with the working fluid at each stage in the contactor, and frictional and viscous forces are considered to be negligible. Likewise, there may be conductive or radiative heat transfers to the air during its residence in the contactor, but these are neglected. Only conductive transfer to the working fluid is considered.

The heat transfer across the boundary layer is given by Fourier's Law:

$$\frac{dQ}{dt} = -k\,a\frac{dT}{dx}$$

For a boundary layer of thickness L, this becomes:

$$\frac{dQ}{dt} = -\frac{k\,a}{L}(T_f - T_a) \tag{8}$$

where T_f is the temperature of the working fluid, T_a is the temperature of the bulk air, and k is the thermal conductivity of stagnant air.

If we take the thermal boundary layer to be the same thickness as the hydrodynamic boundary layer (a good approximation for air [1]), then L in equation 8 can be related to the parameters in equation 5 by:

$$L = \frac{D_{H2O}}{k_{g,H2O}}$$

which, in analogy with equation 7 gives:

$$\left.\frac{dQ}{dC_{H2O}}\right|_{conduction} = \frac{k(T_f - T_a)}{D_{H2O}(C_{H2O} - C_{H2O,vap})} \tag{9}$$

In the fluid, we also have heat from the exothermic formation of $NaHCO_3$:

$$\left.\frac{dQ}{dC_{CO_2}}\right|_{rxn,NaHCO_3} = 110\ \frac{kJ}{mol}$$

and lose heat to the vaporization of water:

$$\left.\frac{dQ}{dC_{H_2O}}\right|_{vaporization} = -44\ \frac{kJ}{mol}$$

We can relate the transfer of heat to a change in temperature by the heat capacity, c_p, and density of air and the working fluid:

$$\frac{dT_{air}}{dQ} = \frac{1}{c_{p,air}\cdot n_{air}}$$

where $c_{p,air} = 29.2\ \frac{J}{K \cdot mol\, air}$ and n_{air} is the density of air in $\frac{mol}{m^3}$. Similarly,

$$\frac{dT_{fluid}}{dQ} = \frac{1}{c_{p,fluid} \cdot n_{fluid}}$$

where $c_{p,fluid} = 75.2\ \frac{J}{K \cdot mol\, fluid}$ (taken to be the same as for pure water) and n_{fluid} is the number of moles of fluid per m^3 of air. n_{fluid} is a parameter that can be adjusted in the conctacting system. It is determined by the concentration of CO_2 collected by the fluid in one pass through the system, and by the efficiency of CO_2 captured from the air. For these calculations, n_{fluid} is set such that 0.9 moles of CO_2 are collected for each mole of NaOH in the fluid during a single pass.

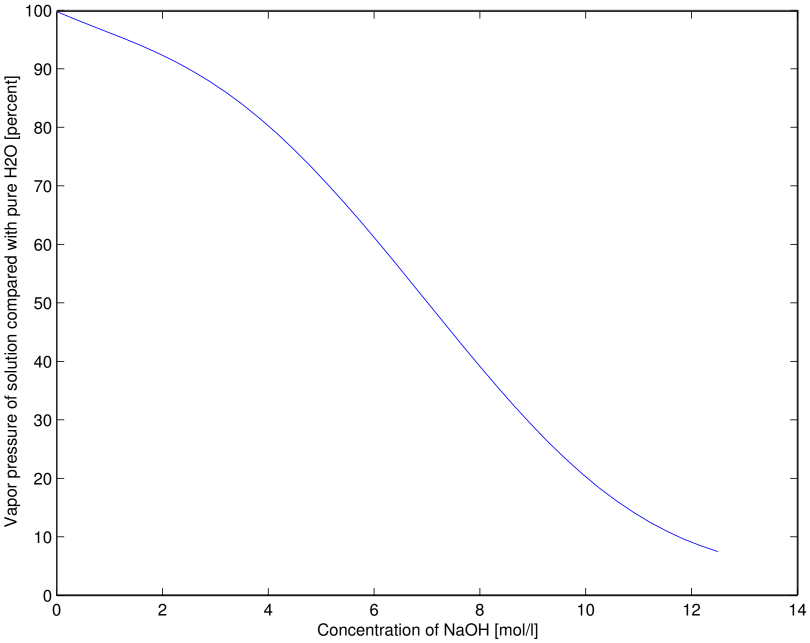
Putting together the above expressions along with Equation 7, we can generate a system of ordinary differential equations, each with C_{CO_2} as the independent variable:

$$\begin{aligned}
\frac{dC_{H_2O}}{dC_{CO_2}} &= 1.5\frac{C_{H_2O} - C_{H_2O,vap}}{C_{CO_2}} \\
\frac{dT_{air}}{dC_{CO_2}} &= \left.\frac{dQ}{dC_{H2O}}\right|_{conduction} \times \frac{dT_{air}}{dQ} \times \frac{dC_{H_2O}}{dC_{CO_2}} \qquad (10) \\
\frac{dT_{fluid}}{dC_{CO_2}} &= \left[\left.\frac{dQ}{dC_{H2O}}\right|_{conduction} \times \frac{dC_{H_2O}}{dC_{CO_2}} + \left.\frac{dQ}{dC_{CO_2}}\right|_{rxn,NaHCO_3} + \left.\frac{dQ}{dC_{H_2O}}\right|_{vaporization} \right] \frac{dT_{fluid}}{dQ}
\end{aligned}$$

B.3 Dependence on [NaOH]

Concentrated NaOH solutions have vapor pressures which are lower than pure water at a given temperature. The vapor pressure of solutions at $25^o c$ is shown in Figure 15

Figure 15: Relative vapor pressure of NaOH solutions at $25^o c$



B.4 Calculations

For a given temperature and relative humidity of the input air as initial conditions, Equations 10 can be integrated numerically to give the mass of H_2O evaporated per mass of CO_2 captured. The system is solved with an explicit finite difference method, with $C_{CO_2,vap}$ calculated at each step using the conditions in the previous step.

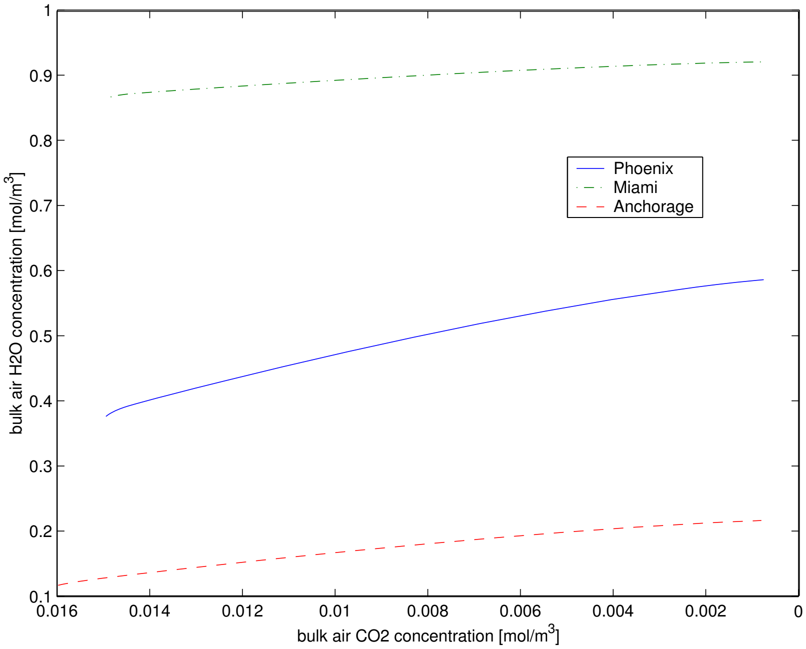
Values for initial conditions reflect the annual average temperature and relative humidity data for three locations: Phoenix, AZ ($T = 21^oC$, $RH = 37\%$), Miami, FL ($T = 23^oC$, $RH = 76\%$), and Anchorage, AK ($T = 2^oC$, $RH = 38\%$).

Since C_{CO_2} is the dependent variable, the limits of integration are the inlet and outlet CO_2 concentrations. The results then depend on the capture efficiency of the contacting unit. A range of efficiencies was used.

B.5 Results

The concentrations during the evolution of a single air parcel are shown in Figure 16. Water is transferred very quickly as the first few percent of CO_2 is captured, then at a slower, stead rate thereafter. This is consistent with the temperature profiles during this evolution, shown in Figure 17 for Phoenix conditions. The temperature of the working fluid drops very quickly as the thermodynamics are dominated by vaporization of water, then reaches a steady state. The air temperature drops slowly and steadily as heat is transferred to the colder working fluid.

Figure 16: Relationship between CO_2 and H_2O with [NaOH]$= 1M$



The results for systems with NaOH concentrations of $0.1M$ and $5M$ are shown in Figures 18 and 19, respectively. Generally, it requires more water to capture CO_2 at higher efficiency, but the effect is not nearly as strong as that of local conditions or solution concentration. The effect of solution concentration is strong enough that, under Miami conditions, a system has *negative* water loss, that is, gains water, when using a $5M$ solution of NaOH. Figure 20 shows the effect of NaOH concentration while holding the capture efficiency constant at 50%.

Figure 17: Temperature evolution of air and working fluid ([NaOH]= $1M$, Phoenix conditions)

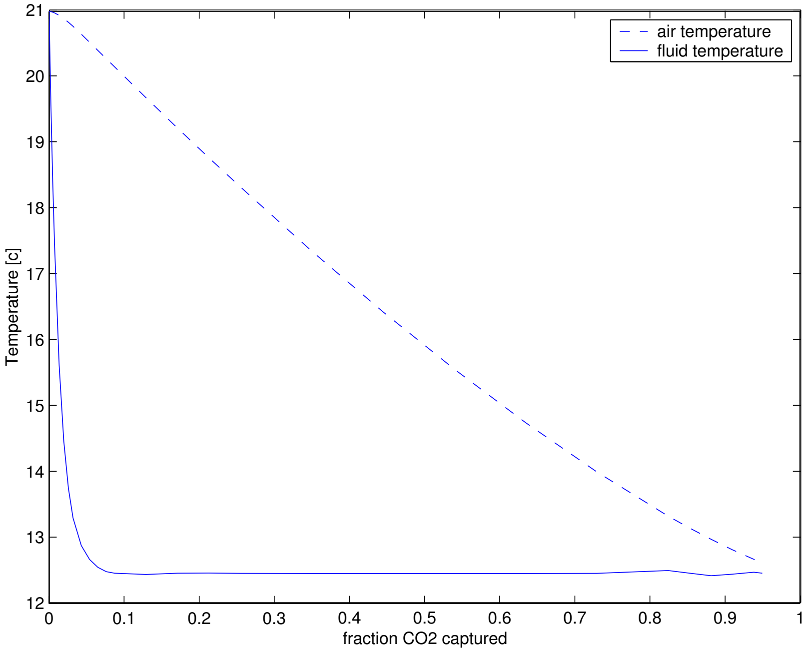


Figure 18: Evaporative water loss with [NaOH] = $0.1M$

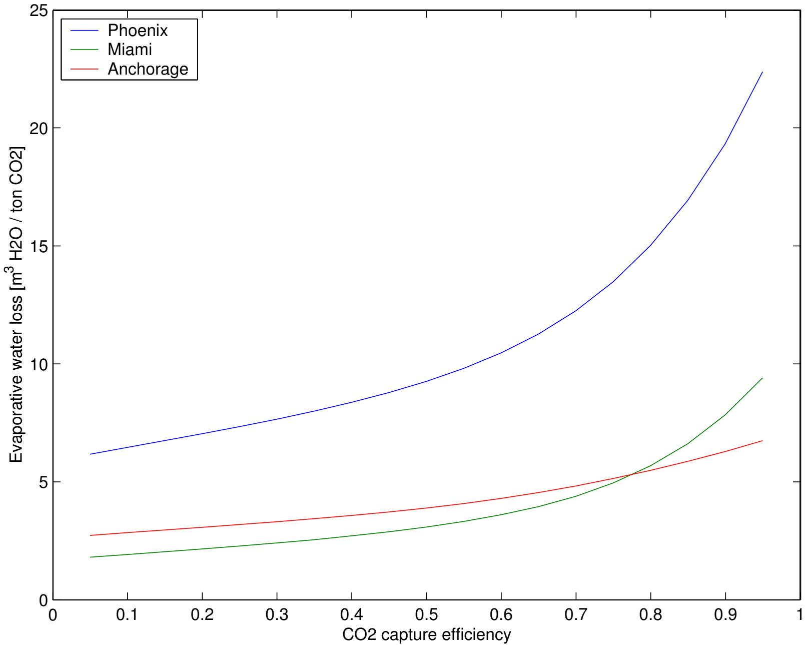


Figure 19: Evaporative water loss with [NaOH] = $5M$

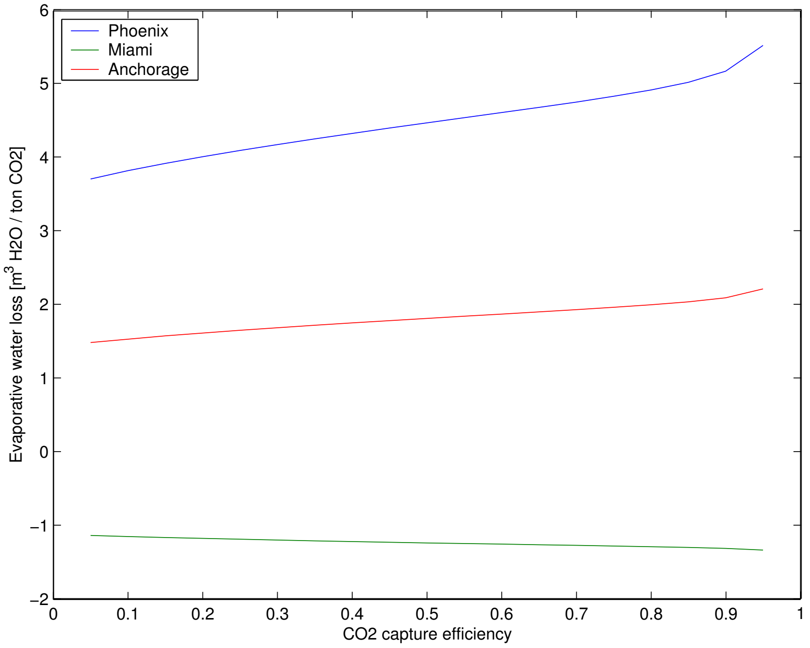


Figure 20: Evaporative water loss for a range of solution concentrations