

*Assessing the Feasibility  
of Capturing CO<sub>2</sub>  
from the Air*

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# Assessing the Feasibility of Capturing CO<sub>2</sub> from the Air

Howard Herzog

## 1. Introduction

The capture of CO<sub>2</sub> from air is a very seductive prospect. If it can be accomplished on a large enough scale and at an affordable price, we have a straightforward approach to stabilize atmospheric CO<sub>2</sub> concentrations. Thus, we can resolve the climate change challenge without disruptive changes to our energy systems or lifestyles.

This paper focuses on non-biological pathways of capturing CO<sub>2</sub> from air. We know biological pathways exist, since plants capture CO<sub>2</sub> from air every day. Terrestrial sequestration of CO<sub>2</sub> through afforestation or reforestation approaches is being actively pursued (Watson *et al.*, 2000). At best, the amount of CO<sub>2</sub> that can be sequestered through these means is limited. Another proposed biological capture method is ocean fertilization. This approach is highly controversial, with questions about its environmental impacts as well as its effectiveness, i.e., whether it can truly sequester the CO<sub>2</sub> that it pulls into the ocean from the air (Buesseler and Boyd, 2003).

Lackner and colleagues at Los Alamos National Laboratory have promoted the idea of “extraction of CO<sub>2</sub> from the atmosphere through engineered chemical sinkage” (Dubey *et al.*, 2002; Lackner *et al.*, 2001; Lackner *et al.*, 1999). They have proposed a prototype system based on using calcium hydroxide as a regenerable sorbent. Lackner, now at Columbia University, claimed in a recent press release that “the cost of trapping carbon dioxide from air could eventually be less than 25 cents per gallon of gas, with the potential for better and cheaper methods in the future” (Columbia University, 2003)<sup>1</sup>. Keith and Ha-Duong (2002) claim “it would be comparatively easy to develop practical air capture technologies on the timescales relevant to climate policy”. They also investigated the calcium hydroxide system and judged “that such a system might plausibly provide air capture at an overall cost of under 200 \$/tC<sup>2</sup> within a few decades”. If these claims are true, they will set a very affordable upper limit on the cost of dealing with climate change. But are they credible? That is the focus of this assessment.

## 2. Industrial CO<sub>2</sub> Capture Processes

There are many commercial processes that can capture CO<sub>2</sub> from a gas stream. The temperature, pressure, and composition of the gas stream are all important criteria for choosing the most appropriate capture process. Experience with removing CO<sub>2</sub> from the air does exist. Air revitalization systems on submarines and space vehicles (Heinrich, 2003) and feed stream treatment for cryogenic air separation plants provide examples.

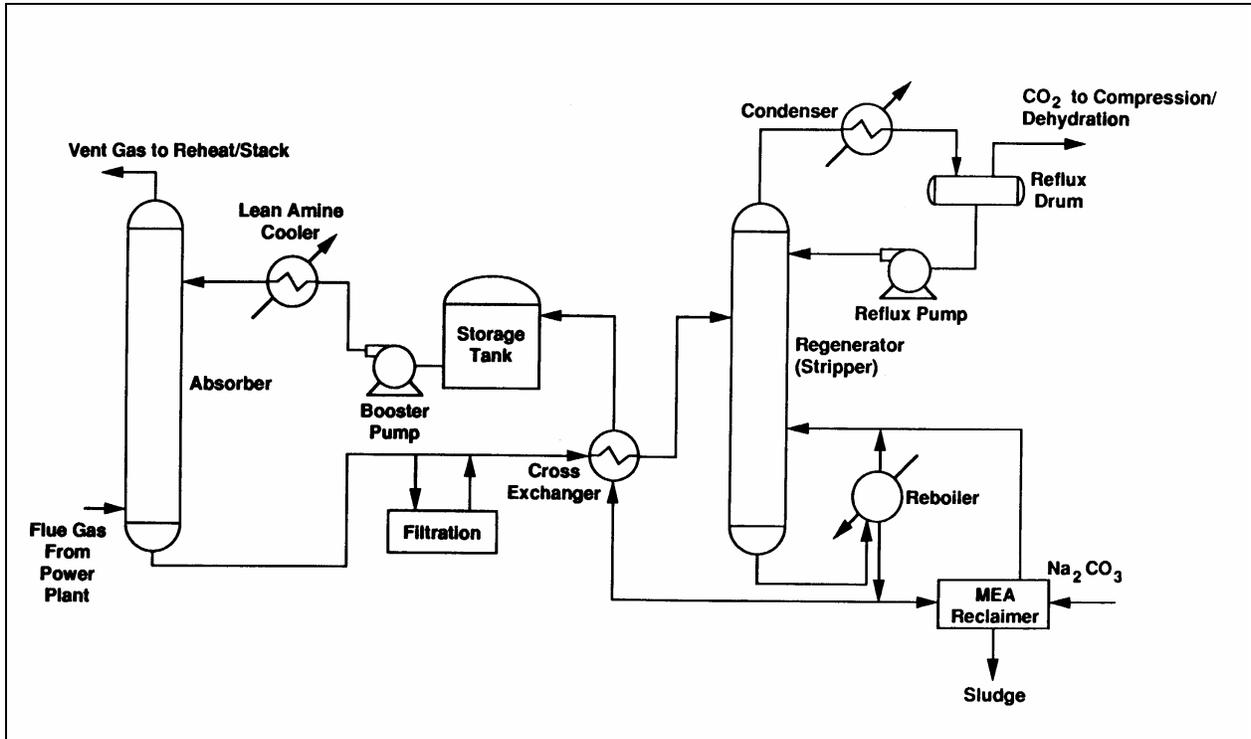
For the capture of CO<sub>2</sub> from power plant flue gas, the preferred process is chemical absorption using monoethanolamine (MEA). Chemical absorption refers to a process where a gas, in this case CO<sub>2</sub>, is absorbed in a liquid solvent by formation of a chemically bonded compound. A

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<sup>1</sup> Note that 25 cents per gallon of gasoline is approximately \$100/tC.

<sup>2</sup> \$/tC represents US dollars per metric ton (tonne) of carbon equivalent. Note that \$1/tC = \$0.27/tCO<sub>2</sub>.

schematic of this process is shown in Figure 1. In the first step of the process, the flue gas is contacted with the MEA in a packed column (i.e., the absorber). The CO<sub>2</sub>-rich MEA solution leaving the absorber is then heated and sent to a stripper, where the CO<sub>2</sub> is removed by steam stripping. The lean MEA is then cooled and recycled back to the absorber.



**Figure 1. Schematic of the MEA process for CO<sub>2</sub> capture.**

There are many criteria when choosing a solvent. To illustrate, below are some criteria to consider when removing CO<sub>2</sub> from a gas stream:

- A solvent that is highly selective to CO<sub>2</sub>. The selectivity of the solvent for CO<sub>2</sub> forms the whole basis of the separation process.
- The carrying capacity of the solvent, i.e., how much CO<sub>2</sub> can be removed per unit of solvent. In general, the less solvent required, the better (less pumping costs, smaller equipment sizes, etc.).
- The energy and conditions required to drive off the CO<sub>2</sub> and regenerate the solvent. The lower the regeneration energy, the better. Also, for temperature swing processes like MEA, the lower the regeneration temperature the better.
- The composition of the gas stream. Certain components in the gas stream may poison the solvent (i.e., make it ineffective) or cause operational problems like foaming.

Why is MEA the preferred process for removing CO<sub>2</sub> from flue gases? The low partial pressure of CO<sub>2</sub> in the flue gas (0.03-0.15 atm) is a key factor. At these low partial pressures, MEA has

reasonable solvent loadings. Though the regeneration energy requirement is significant, it is lower than alternatives such as various carbonate processes.

When producing power from an Integrated Gasification Combined Cycle (IGCC) power plant, CO<sub>2</sub> can be captured from a synthesis gas prior to combustion. The high CO<sub>2</sub> partial pressure in the synthesis gas opens up more solvent options, such as using Selexol (a physical solvent). At low partial pressures, the solvent loadings for these physical solvents are unacceptable. However, solvent loadings are acceptable at higher partial pressures. The benefit of these physical solvents over MEA is the much lower regeneration energy requirement. In the Selexol process, the gas stream is contacted with the solvent in an absorber at elevated pressures. The pressure of the CO<sub>2</sub>-rich solvent is then reduced to release the CO<sub>2</sub>, with the lean solvent being pumped back to the absorber.

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**Table 1. Comparison of the MEA and Selexol processes.**

<b>Power Plant</b>	<b>Capture Process</b>	<b>CO<sub>2</sub> PP (atm)</b>	<b>Avoided Cost (\$/tC)</b>
Coal Gasification (IGCC)	Selexol	18.8	95
Pulverized Coal (PC)	MEA	0.11	180

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A comparison of these two CO<sub>2</sub> capture processes is shown in Table 1 (David and Herzog, 2000). The cost is given in \$/tC avoided, which takes into account any additional CO<sub>2</sub> generated by the capture process -- usually as a direct result of energy usage in the capture process. In the capture of CO<sub>2</sub> from a power plant, this energy usage usually manifests itself by a de-rating of the power plant (lowering the amount of electricity produced per unit of fuel input). This de-rating is commonly referred to as the energy penalty<sup>3</sup>, which strongly correlates with the avoided cost<sup>4</sup>.

The IGCC/Selexol process has a much lower energy penalty than the PC/MEA process primarily for two reasons. First, the energy needed to regenerate the solvent is much less<sup>5</sup>. An energy penalty of a few percent is required to regenerate the Selexol, while MEA requires roughly a 20% energy penalty (assuming back-pressure steam is used). Second, the PC/MEA process

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<sup>3</sup> The energy penalty can be calculated as  $(x-y)/x$ , where x is the net output in kW of a reference power plant without capture and y is the net output in kW of the same plant with capture. The calculation requires that the same fuel input be used in both cases. For example, if the net power plant output is reduced by 20% because of the capture process ( $y=.8x$ ), the process is said to have an energy penalty of 20%.

<sup>4</sup> Captured cost is the incremental cost due to capture divided by the total amount captured. Avoided cost is the difference in cost per net kWh output (with and without capture) divided by the difference in emissions per net kWh (without and with capture). For processes that capture 100% of the CO<sub>2</sub>, it can be shown that Avoided Cost = Captured Cost / (1 – Energy Penalty).

<sup>5</sup> The energy required to break the CO<sub>2</sub>-MEA bond is greater than that to break the CO<sub>2</sub>-Selexol bond. Also, the low pressure MEA process requires a temperature swing regeneration process, as compared to a less energy intensive pressure swing regeneration process for Selexol.

requires more energy to move the gas stream through the absorber<sup>6</sup>. To process the same amount of CO<sub>2</sub>, the PC/MEA process must handle 170 times more gas by volume than the IGCC/Selexol process. Therefore, to overcome the absorber pressure drops in the PC/MEA process requires about a 2-3% energy penalty, as opposed to a very small energy penalty (near zero) in the IGCC/Selexol process.

Both of the reasons for reduced energy penalty (and, by correlation, the avoided costs) of the IGCC/Selexol process over the PC/MEA process are related to the partial pressure of CO<sub>2</sub> in the gas stream. A high CO<sub>2</sub> partial pressure allows the use of the IGCC/Selexol process, meaning lower regeneration energy requirements. Also, the higher CO<sub>2</sub> partial pressure reduces the air handling requirements, resulting in much lower pressure drops.

By extrapolation of this correlation with partial pressure, we can get an initial assessment of a process to capture CO<sub>2</sub> from air. The partial pressure of CO<sub>2</sub> in air is 0.00038 atm. Because of this very low partial pressure in air, a solvent like calcium hydroxide is suggested (see Heinrich, 2003 or Dubey *et al.*, 2002). But the heat of reaction to break the CO<sub>2</sub>-calcium hydroxide bond is over twice that of the CO<sub>2</sub>-MEA bond. In addition, Ca(OH)<sub>2</sub> requires a much higher regeneration temperatures (up to 1500°C vs. 120°C for MEA). The low partial pressure in air also means that, for each unit of CO<sub>2</sub> removal, about 300 times as much vapor must be processed compared to the PC/MEA process (or 50,000 times that of the IGCC/Selexol process). Therefore, from both air handling and solvent regeneration considerations, we should expect a much higher energy penalty for capture from air than for the PC/MEA process. Since costs generally correlate with the energy penalty in a highly non-linear way, one would expect the cost of air capture to be significantly higher than the \$180/tC shown for the amine process in Table 1. This analysis seems at odds with Lackner's 25 cents a gallon and Keith/Ha-Duong's \$200/tC. To try to understand this difference better, a more detailed analysis is required.

### 3. Air Capture – Solvent Regeneration

Both Lackner and Keith/Ha-Duong base the regeneration system on the CaO-CaCO<sub>3</sub> system. In a personal communication (March 16, 2003), Lackner states:

“A big cost of the extraction of CO<sub>2</sub> from air will be the recovery of the sorbent material .... Lime calcination can be done for about \$10 to \$15 per ton of CO<sub>2</sub>. It would therefore dominate the cost of the process. Multiplying this number by two, to acknowledge that the system will have additional parts, one finds a cost of maybe \$30 per ton of CO<sub>2</sub> (\$110 per ton of carbon).”

This initial analysis cannot be taken literally because the regeneration of the sorbent material is not simply lime calcination. In lime calcination, the primary product is CaO, not CO<sub>2</sub>. In lime calcinations, the CaCO<sub>3</sub> is heated to 1500°C in a natural gas-fired kiln in order to drive off the CO<sub>2</sub>. Because this CO<sub>2</sub> is diluted by the combustion gases, the off-gas of the kiln ranges from 14-33% CO<sub>2</sub> (Hendriks *et al.*, 1999), not the 90% plus that usually defines CO<sub>2</sub> capture. The cost and energy penalty of a calcination process that produces high purity CO<sub>2</sub> will be significantly greater than a standard lime calcination process.

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<sup>6</sup> The absorbers contain packing to ensure good gas-liquid contacting. This contacting is required for the CO<sub>2</sub> to be absorbed from the gas phase by the solvent. Energy must be provided to overcome the pressure drops associated with moving the gas through the packing.

A solution to this problem, as suggested by Lackner (personal communication March 30, 2003) and Keith and Ha-Duong (2002), is to use pure oxygen instead of air in the calciner. This satisfies the capture criterion of producing high purity CO<sub>2</sub> because the off-gas is primarily CO<sub>2</sub> and water, with the water easily separated during compression. In addition, the CO<sub>2</sub> produced by the natural gas now gets captured along with the CO<sub>2</sub> released by the CaCO<sub>3</sub>, meaning that we do not need to subtract off the CO<sub>2</sub> generated by the natural gas burned in the kiln in the avoided cost calculation. However, this is no longer a standard lime calcination system. In Appendix A we estimate that the avoided cost is \$480/tC.

In doing our calculations in Appendix A, we wanted to generate as low an avoided cost estimate as we realistically could. Therefore, we used the most optimistic values we could justify for fuel use, oxygen cost, excess oxygen, etc. Still, our estimate was much larger than Lackner's or Keith/Ha-Duong's estimate. In Appendix B, we attempt to reconcile the differences in these estimates. Our analysis shows that the critical assumptions that give rise to these differences are:

1. Lackner assumes a dry kiln with a thermal efficiency of 80%. Hendriks *et al.* (1999) state that "a modern dry kiln ... has an efficiency of 60%".
2. Lackner claims that "there is sufficient low grade heat to perform operations like drying the wet calcium carbonate". Our analysis indicates otherwise. We conclude that the calcium carbonate entering the kiln will have a high moisture content. This will further reduce the efficiency of the kiln. According to Hendriks *et al.* (1999), the most efficient kilns with wet feeds will have an efficiency of about 33%.
3. Lackner uses a *delivered* natural gas price of \$3/GJ, while we use \$4/GJ (a value which we feel may still be too optimistic).
4. Lackner uses an oxygen price of \$11-12 per ton O<sub>2</sub>. We used \$27 per ton O<sub>2</sub>, based on conversations with a large industrial gas supplier.
5. Lackner does not explicitly take into account the other cost components, such as compression, recycling flue gas from calciner, etc.
6. Lackner does not take into account the extra CO<sub>2</sub> produced by the energy requirements associated with oxygen production, CO<sub>2</sub> compression, and process auxiliaries (e.g., pumps, blowers, etc.). We estimate that this amount of CO<sub>2</sub> generated would be about 20% of the CO<sub>2</sub> captured from air.

In defending his cost estimate, Lackner argues that one must account for technological change that will reduce future costs. For instance, what if there were a new solvent that was much more energy efficient? This outlook is warranted when initiating research programs trying to develop such a solvent or even setting cost goals. However, one cannot reliably provide cost estimates on what does not exist today and may not exist in the future.

We do not want to get into a debate on costs of future technologies and resource prices. In Appendix A, we have laid out the cost estimates in a transparent manner, so the readers of this report can make up their own minds whether future costs of 100-200 \$/tC are credible relative to the estimate derived here of \$480/tC. In any case, even at \$480/tC, the regeneration costs may be affordable to solve the problem. After all, this is only a \$1.20 per gallon gas tax – large by US standards, but not by European standards. It is potentially affordable and probably not a showstopper. However, as discussed in the next section, the absorption system may be a showstopper.

#### 4. Air Capture – Absorption

In his personal communication of March 16 (2003), Lackner claims that lime calcination will “dominate the cost of the process.” Keith and Ha-Duong (2002) agree, claiming the “absorber system would be only ¼ to 1/10 the cost of the calciner.” Yet, neither group does any design calculations for an absorber system to support such claims. It is our opinion that both of these groups have grossly underestimated the challenges of absorbing CO<sub>2</sub> from the air. Below we lay out the basis for this opinion.

Neither Lackner nor Keith and Ha-Duong provided a description of an absorption system in any detail. Therefore, we could not comment on a specific design. Since there are many possibilities in the way one can approach this problem, we decided to start by analyzing two limiting cases. One limit is to use standard absorber systems (as shown in Figure 1). This results in a “minimum volume system”. The other limit is to use open ponds, which results in a “minimum pressure drop system”.

**Minimum volume system.** For CO<sub>2</sub> capture from power plant flue gas, the standard practice is to use an absorber system (see Figure 1). Similar systems can theoretically be used to capture CO<sub>2</sub> from air. The absorbers contain “packing” in order to create the large amount of vapor-liquid contacting area required. This is important in realizing the typical design goal of keeping equipment volumes as small as practical, which is why we refer to this case as our “minimum volume system”. Minimizing the absorber volume tends to minimize its cost of construction, which is a major element of overall cost. Another of the major costs associated with these relatively compact systems is the energy needed to force the CO<sub>2</sub>-laden vapor stream through the absorber. This energy requirement manifests itself as a pressure drop in the vapor stream, with the exact magnitude a function of the detailed absorber design, including the type of packing one chooses.

It is a straightforward task to estimate the magnitude of the pressure drop in an air capture system. Based on a review of engineering studies in the literature for the capture of CO<sub>2</sub> from a power plant flue gas using the amine process, the energy penalty associated with the pressure drop in the absorber is in the range of 2-4% of the plant output. As discussed in section 2, to capture the same amount of CO<sub>2</sub> as the PC/MEA flue gas process, the air capture process needs to handle 300 times more volume of gas. Since the energy penalty scales linearly with the volumetric flow rate<sup>7</sup>, a first cut at the energy penalty resulting from the absorber pressure drop

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<sup>7</sup> This assumes that the pressure drop in the absorber will remain unchanged. This constant pressure drop assumption is valid if linear velocities in the absorber are unchanged. For a 300-fold increase in the volumetric flow

in an air capture system is 600-1200%. An energy penalty over 100% will render the process infeasible (creating more CO<sub>2</sub> than it captures), while practical reasons (e.g., cost) will almost certainly require this energy penalty to be much less. While there are realistic expectations that one can reduce this 600-1200% range significantly in the design process, we doubt very much whether it can be reduced to an acceptable level.

It is our conclusion that the use of a traditional absorber system will result in unacceptably large pressure drops, making this system is not feasible for air capture. The large pressure drops are strongly linked to the large amount of air that must be processed. It is important to point out that neither Lackner nor Keith and Ha-Duong proposed using a traditional absorber system. However, we needed to do this analysis to provide one of two pillars that support our final conclusions.

**Minimum pressure drop system.** Since the major barrier in the above analysis was the high pressure drop, we decided to analyze the opposite extreme – a no pressure drop system. In this case, one can imagine CO<sub>2</sub> diffusing through the air into a large “lake” of solvent. The mechanisms for transfer consist of CO<sub>2</sub> diffusing through the air to the surface of the lake, establishing an equilibrium at the lake’s surface between the CO<sub>2</sub> concentration in each phase, the CO<sub>2</sub> diffusing away from the surface through the liquid, and finally the CO<sub>2</sub> reacting with the solvent. The literature is very clear that the rate limiting step in the above mechanism is mass transfer in the liquid phase (see Appendix C). In Appendix C, we estimate the flux of CO<sub>2</sub> from the air into the solvent as  $1.3 \times 10^{-6}$  mols/s/m<sup>2</sup>. Lackner *et al.* (1999) do a similar calculation and report a flux of  $4 \times 10^{-4}$  mols/s/m<sup>2</sup>. One reason that Lackner *et al.* (1999) reports transport rates over 300 times what we calculate is that they assume that gas phase mass transfer is limiting. However, based on our reading of the literature, this assumption seems indefensible<sup>8</sup>.

We can now calculate the surface area required in this case. Our flux is equivalent to  $1.8 \times 10^{-6}$  Gt CO<sub>2</sub>/yr/km<sup>2</sup>. In 2001, the United States emitted 1.58 GtC (or about 5.8 Gt CO<sub>2</sub>). Therefore, the surface area required to absorb all of these emissions is about 320,000 km<sup>2</sup>. This is about one-third of the total US surface area!

**Real Systems.** Obviously, neither of the two limiting cases we describe above is practical. At one extreme we have unacceptable pressure drops. At the other extreme, we have unacceptable surface areas. The real question is whether we can find a practical design somewhere in the middle. Given the results we get from the limiting cases, it is our opinion that this task is extremely difficult at best, and may be infeasible even with improved solvent technology.

This conclusion is based on the trade-off between pressure drop and area. It seems that to produce a design with acceptable pressure drops will result in devices with large areas. This will not only lead to large costs (much larger than the suggested “fraction of the regeneration costs”), but also raises questions like how one uniformly distributes and collects the solvent over large surface areas. More detailed analysis could be carried out if proponents of this technology suggest a specific design for the process.

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for the air capture process, this constant pressure drop constraint requires a 17-fold increase ( $\sqrt{300}$ ) in absorber cross-sectional area. This will lead to about an order of magnitude increase in the capital cost for the absorbers.

<sup>8</sup> Lackner *et al.* (1999) base their assumption on some simple laboratory experiments they conducted.

## 5. Conclusions

Being able to capture CO<sub>2</sub> from air at a large scale and affordable price would have profound effects on climate change policy. Unfortunately, we are a long way from achieving this goal. It is feasible to capture CO<sub>2</sub> from air – plants do it all the time. At present, this biological pathway is the state-of-the-art.

Proposals have been made to use industrial separation technology to capture CO<sub>2</sub> from air. Based on our analysis of these concepts, we do not believe that this is a productive or cost-effective approach if one is limited to existing separation techniques (e.g., chemical solvents). We have found that the papers presented on this topic in the literature have inadequately addressed the critical issue of what a practical absorption system would look like and have used overly optimistic (and at times unrealistic) parameters in their calculations.

However, we fully agree with the proponents of capturing CO<sub>2</sub> from air that its pursuit is a worthwhile endeavor. However, instead of an effort in applied research, we feel that this must be treated as a basic research effort, with emphasis on developing new separation technologies that would be appropriate to the unique features of capturing CO<sub>2</sub> from air.

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## Appendix A. Estimating the Cost of Solvent Regeneration

In this Appendix, we estimate the cost of a lime regeneration system that burns oxygen instead of air, so as to produce a high purity CO<sub>2</sub> stream that can be sequestered.

We focus on three major components of this system: the capital cost of the calciner, the cost of oxygen, and the cost of fuel (i.e., natural gas).

1. Keith and Ha-Duong (2002) claim “the capital cost of the calciner is around 1000\$ for each kg-CO<sub>2</sub>/hr of capacity.” Assuming 8000 hrs/yr operation and a fixed charge rate of 15% to annualize this capital cost, the calciner costs \$19/tCO<sub>2</sub>.
2. Hendriks *et al.* (1999) state that the “fuel use in a wet kiln may vary between 5.3 and 7.1 GJ/tonne clinker”. We must use a wet kiln since the clinker (i.e., CaCO<sub>3</sub>) is precipitated from aqueous solution. For our analysis, we will use the lower value for fuel use, 5.3 GJ/tonne clinker or about 12 GJ/tCO<sub>2</sub>. Taking natural gas delivered at \$4/GJ, the cost of fuel is \$48/tCO<sub>2</sub>.
3. Based on a fuel use of 12 GJ/tCO<sub>2</sub> (530 kJ/mol CO<sub>2</sub>), the stoichiometric amount of O<sub>2</sub> required is 1.32 moles O<sub>2</sub> per mole CO<sub>2</sub> captured from air<sup>9</sup>. This corresponds to 0.96 tonnes O<sub>2</sub> per tonne CO<sub>2</sub>. At \$27 per tonne for oxygen<sup>10</sup>, the oxygen cost is \$26/tCO<sub>2</sub>.

Just based on the above 3 items, the cost is \$93/tCO<sub>2</sub> or \$340/tC. However, there are other significant cost components that still need to be included:

- a. The CO<sub>2</sub> still must be compressed. This includes capital costs (see item f below) and energy costs (see item d below).
- b. Since the CO<sub>2</sub> produced from fuel use in the kiln will be collected along with the CO<sub>2</sub> driven off from the clinker, we do not have to account for this as an energy penalty. However, it increases the amount of CO<sub>2</sub> that needs to be compressed by 66%, which must be accounted for<sup>11</sup>.

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<sup>9</sup> Based on the lower heating value of CH<sub>4</sub> of 192 kcal/mol (800 kJ/mol) and the requirement of 2 mols O<sub>2</sub> per mol CH<sub>4</sub> (no excess oxygen).

<sup>10</sup> Based on conversations with a large industrial gas supplier. Range for a large (350-500) ton per day plant producing oxygen as a gas (GOX) is 11-14 cents per scf of O<sub>2</sub>. We used the low end of the range for our calculation.

<sup>11</sup> From points 2 and 3 above, the fuel use in the kiln is 530kJ/mol CO<sub>2</sub>. The heating value of methane is about 800 kJ/mol. This would require about .66 mols of methane (producing .66 mols of CO<sub>2</sub>) for each mole of CO<sub>2</sub> recovered.

- c. There are CO<sub>2</sub> emissions associated with oxygen production. Assuming a natural gas combined cycle power plant produces the electricity of the oxygen plant, these emissions would equal 8% of the amount of CO<sub>2</sub> captured from air<sup>12</sup>.
- d. The energy requirement for compression would be about 0.11 kWh/kg CO<sub>2</sub> (based on our analysis of engineering studies in the literature). At a heat rate of 6680 kJ/kWh and a fuel cost of \$4/GJ, the fuel cost for compression is \$2.9/tCO<sub>2</sub> compressed or about \$5/tCO<sub>2</sub> captured from air (see point b above). In addition, there are CO<sub>2</sub> emissions associated with this electricity use. Once again, assuming a natural gas combined cycle power plant produces the electricity, these emissions would equal 7% of the amount of CO<sub>2</sub> captured from air.
- e. Other energy is required to rotate the kiln, handle the solids, recycle flue gas. The emissions associated with this energy use could easily be another 5% of the amount of CO<sub>2</sub> captured from air (based solely on our engineering judgment).
- f. Capital costs are needed for filtering the clinker, CO<sub>2</sub> compression, the recycling of some of the flue gas from the kiln, etc. We can estimate the compressor costs at about \$13 per tCO<sub>2</sub>/yr. Multiplying by 2 to account for other items and multiplying by 1.66 (see point b above) and annualizing at 15%/yr, we estimate a cost of \$6.5/tCO<sub>2</sub>.

Now, redoing the overall calculation:

$$\$93/\text{tCO}_2 \text{ (items 1-3)} + \$5/\text{tCO}_2 \text{ (item d)} + \$6.5/\text{tCO}_2 \text{ (item f)} = \$105.5/\text{tCO}_2 = \$383/\text{tC}$$

Accounting for the excess CO<sub>2</sub> emissions from points c, d, and e above, we estimate the overall cost to be  $383/(1-.08-.07-.05) = \$480/\text{tC}$ .

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<sup>12</sup> Based on an energy requirement for the oxygen plant of 220 kWh/tonne O<sub>2</sub>, an oxygen requirement of 1.32 mols O<sub>2</sub> per mol CO<sub>2</sub> captured from air (see point 3 above), and a natural gas power plant with an emissions factor of 0.37 kg CO<sub>2</sub>/kWh.

## Appendix B. Reconciling the Cost of Solvent Regeneration

In this Appendix, we try to reconcile the differences between our calculations in Appendix B for the cost of solvent regeneration and the estimates of Lackner and Keith/Ha-Duong. Using information from Lackner's personal communication (March 30, 2003), one can actually reconcile the differences fairly well. Key points include:

1. Lackner claims that "there is sufficient low grade heat to perform operations like drying the wet calcium carbonate". The primary source of this heat is what Lackner refers to as the "hydroxylation" reaction ( $\text{CaO} + \text{H}_2\text{O}$ ). We find this claim unsupportable because the heat of "hydroxylation" is small (65 kJ/mole) compared to the difference in heat requirements between a wet and a dry kiln (minimum of 150 kJ/mole)<sup>13</sup>. Given that drying processes are very energy inefficient, we conclude that the amount of low grade heat available is totally inadequate.
2. Lackner uses a kiln efficiency of 80%. This number is not based on actual experience. Hendriks *et al.* (1999) state that "a modern dry kiln ... has an efficiency of 60%".
3. Lackner uses a natural gas price of \$3/GJ, while we use \$4/GJ. According to the DOE's Energy Information Agency ([www.eia.doe.gov](http://www.eia.doe.gov)), the average 2001 *wellhead* price was \$4.12/Mcf (Mcf = thousand cubic feet) or \$3.89/GJ. Given that they project the 2020 price to be \$3.70/Mcf and the 2025 price to be \$3.90/Mcf and that the delivered price could easily add \$1-2/GJ, we feel that even our \$4/GJ number is quite optimistic. Note that if we used \$5/GJ as our gas price in Appendix A, the regeneration cost would have risen from \$480/tCO<sub>2</sub> to \$540/tCO<sub>2</sub>.
4. Lackner uses an oxygen price of \$11-12 per ton O<sub>2</sub>. We use \$27/ton based on information supplied by a large industrial gas supplier.
5. Lackner does not take into account the other cost components we list in Appendix B.

We can now redo the cost calculations using Lackner's assumptions. The calciner would still cost \$19/tCO<sub>2</sub>. The energy requirement is only 2.2 GJ/tonne clinker (5 GJ/tCO<sub>2</sub>), requiring 0.55 tonnes O<sub>2</sub> per tonne CO<sub>2</sub>. The gas at \$3/GJ is \$15/tCO<sub>2</sub> and the oxygen is about \$6/tCO<sub>2</sub>. We ignore items a-f in Appendix A. Summing this up yields \$40/tCO<sub>2</sub> or about \$150/tC, in-line with the \$100-200/tC estimates quoted above.

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<sup>13</sup> The primary difference between the wet and dry kiln is the need to evaporate water.

## Appendix C – Estimating the Flux of CO<sub>2</sub> into a Solvent Lake

The problem of estimating the overall mass transfer flux of CO<sub>2</sub> into a “lake” saturated with Ca(OH)<sub>2</sub> relies on finding the correct interfacial mass transfer coefficients. The most common representation of the gas-liquid mass transfer process involves a gas-side film model combined with a liquid-side film model. Assuming a very large pool of saturated absorbent, at steady state, the mass transfer flux of CO<sub>2</sub> may be written [Danckwerts, p. 146]:

$$J_{CO_2} = k_G^\circ(p - p_i) = Ek_L^\circ(A^* - A^\circ) \quad (1)$$

where:  $J_{CO_2}$  is the overall mass transfer flux of CO<sub>2</sub>, mol·m<sup>-2</sup>·s<sup>-1</sup>  
 $k_G^\circ$  is the gas-side mass transfer coefficient, mol·m<sup>-2</sup>·atm<sup>-1</sup>·s<sup>-1</sup>  
 $k_L^\circ$  is the liquid-side mass transfer coefficient, m·s<sup>-1</sup>  
 $p$  is the partial pressure of CO<sub>2</sub> in atmosphere, atm  
 $p_i$  is the partial pressure of CO<sub>2</sub> at interface, atm  
 $A^*$  is the molar concentration of CO<sub>2</sub> at interface, mol·m<sup>-3</sup>  
 $A^\circ$  is the bulk molar concentration of CO<sub>2</sub>, mol·m<sup>-3</sup>  
 $E$  is the reaction enhancement factor<sup>14</sup>

One of the first issues is that  $p_i$  and  $A^*$  are not easily measurable. Their values adjust such that equation (1) is valid. In addition, it is normally assumed that equilibrium exists at the interface. A more useful expression for the flux may therefore be obtained [Danckwerts, p. 147] that involves only  $p$  and  $A^\circ$ , bulk concentrations in the gas and liquid phase, respectively.

$$J_{CO_2} = K_G(p - HeA^\circ) = K_L\left(\frac{p}{He} - A^\circ\right) \quad (2)$$

where:  $He$  is the Henry constant for the air-CO<sub>2</sub>-H<sub>2</sub>O system, atm·m<sup>3</sup>·mol<sup>-1</sup>  
 $K_G$  is the overall mass transfer coefficient based on gas phase, mol·m<sup>-2</sup>·atm<sup>-1</sup>·s<sup>-1</sup>  
 $K_L$  is the overall mass transfer coefficient based on liquid phase, m·s<sup>-1</sup>

A comparison of equations (1) and (2) shows that  $K_L$  can be expressed as [adapted from Danckwerts, p. 147, eqn. 5-171]:

$$\frac{1}{K_L} = \frac{1}{Ek_L^\circ} + \frac{1}{Hek_G^\circ} \quad (3)$$

<sup>14</sup> The reaction of CO<sub>2</sub> with HO<sup>-</sup> in the liquid phase may enhance the overall mass transfer of CO<sub>2</sub> by several fold. In order to account for this effect, an enhancement factor  $E$  is introduced [Danckwerts, p. 34].  $E$  is the ratio between the absorption flux when reaction occurs to that which would occur if there were no reaction.

For the air-CO<sub>2</sub>-H<sub>2</sub>O-Ca(OH)<sub>2</sub> system, the literature is very clear that the liquid side mass transfer is limiting, i.e.,  $He k_G \gg Ek_L$  (see Iliuta *et al.*, 1997). Therefore, from equation (3), we conclude that  $K_L \cong Ek_L^\circ$  and the overall mass transfer flux of CO<sub>2</sub> (see equation (2)) becomes:

$$J_{CO_2} = Ek_L^\circ \left( \frac{p}{He} - A^\circ \right) \quad (4)$$

The terms in this equation were calculated as follows:

1. Since Ca(OH)<sub>2</sub> is a strong base, most of the CO<sub>2</sub> in the solution will exist as CO<sub>3</sub><sup>2-</sup> or HCO<sub>3</sub><sup>-</sup> ions, implying that  $A^\circ \approx 0 \text{ mol}\cdot\text{L}^{-1}$ . Based on the solubility product of Ca(OH)<sub>2</sub> and the acidity constants of H<sub>2</sub>CO<sub>3</sub>, the pH of the resulting solution is  $\approx 10$ .
2. Partial pressure of CO<sub>2</sub> in the atmosphere is approximately<sup>15</sup>  $4 \cdot 10^{-4} \text{ atm}$ .
3. At 298 K, the Henry's law constant for the CO<sub>2(g)</sub>/H<sub>2</sub>O<sub>(l)</sub> system is 30.84 atm·L·mol<sup>-1</sup> [NIST Database] which results in a dissolved CO<sub>2</sub> concentration, at the interface, of  $1.3 \cdot 10^{-5} \text{ mol}\cdot\text{L}^{-1}$  or  $1.3 \cdot 10^{-2} \text{ mol}\cdot\text{m}^{-3}$ .
4. The reaction of CO<sub>2</sub> with the alkaline solution may enhance the overall mass transfer coefficient several fold. The rate limiting reaction is the conversion of CO<sub>2</sub> to carbonate ions in the presence of HO<sup>-</sup> [Astarita, p. 132]. Enhancement factors have been published by Danckwerts<sup>16</sup> for a range of liquid-side mass transfer coefficients [1].
5. The liquid-side mass transfer coefficient,  $k_L^\circ$ , depends on the interaction between the air and the liquid phase. For air-ocean carbon dioxide exchange, Jähne and Haußecker have published values of  $k_L^\circ$  ranging from  $10^{-6}$  to  $10^{-4} \text{ m}\cdot\text{s}^{-1}$  [4]. The exact value depends on the wind velocity, which in turn controls the residence time of a fluid "packet" at the interface. This residence time also dictates the magnitude of the enhancement factor,  $E$  [Danckwerts, p. 241, fig. 10-1]. Thus, the enhancement factor is a function of  $k_L^\circ$ .

Qualitatively, the time constant for physical transport is given by  $\frac{D_{CO_2}}{k_L^{\circ 2}}$ . For the largest reasonable value of  $k_L^\circ$  ( $10^{-4} \text{ m}\cdot\text{s}^{-1}$ ) and with  $D_{CO_2} = 1 \cdot 10^{-9} \text{ m}^2\cdot\text{s}^{-1}$ , this gives a time constant of 0.1 seconds. The relevant chemistry is:



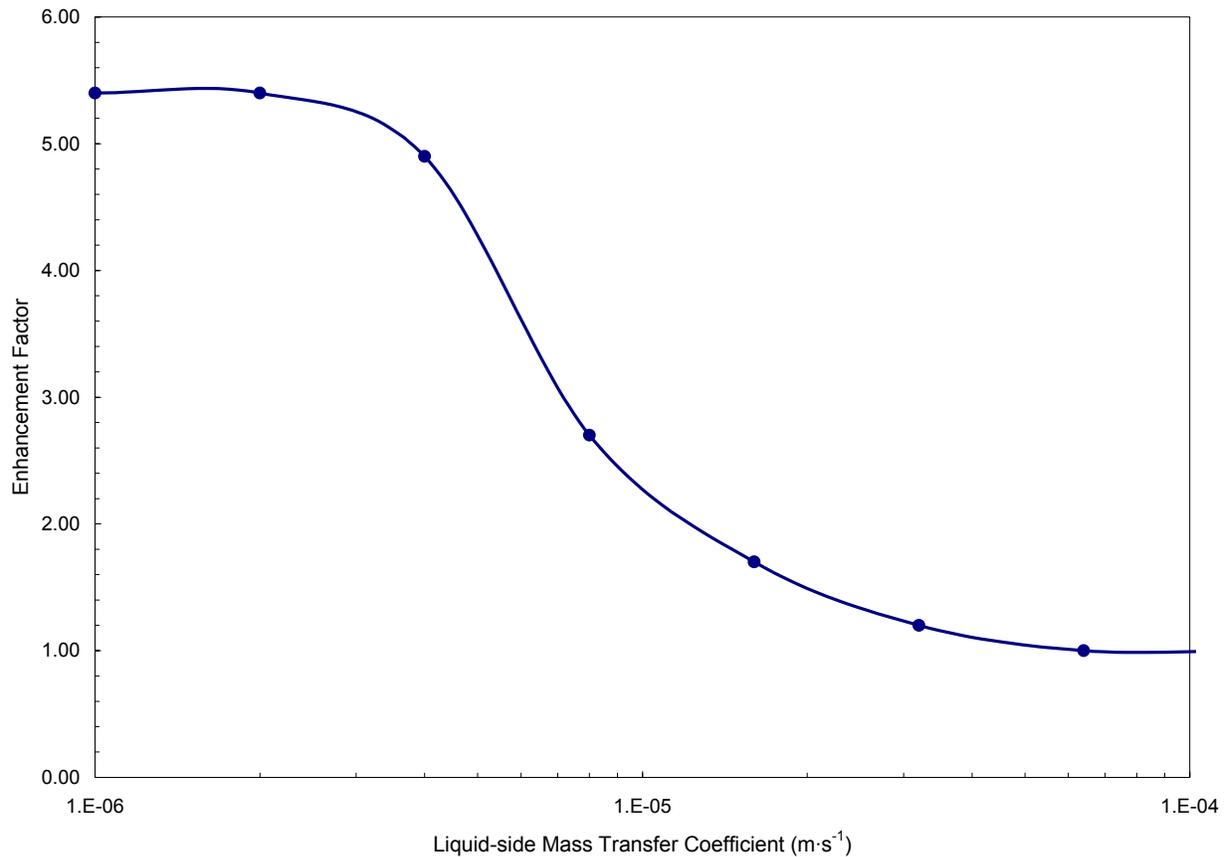
<sup>15</sup> Corresponding to a molar fraction of approximately 400 ppm.

<sup>16</sup> Page 241, fig. 10-1.

for which the rate expression is known to be:

$$\dot{r} = k_d[CO_2][HO^-] \quad (6)$$

The value of  $k_d$  at 25 °C [Danckwerts, p. 24 and Astarita, p. 145] is about  $1 \cdot 10^4 \text{ L} \cdot \text{mol}^{-1} \text{ s}^{-1}$ . Thus, a characteristic time for this reaction is  $\{k_d[HO^-]\}^{-1}$ , or about 1.0 second. Since the chemistry is much slower than the physical transport for the largest value of  $k_L^\circ$ , no enhancement is expected in this case. A more quantitative result, based on Figure 10-1 of Danckwerts, is shown in the figure.



**Figure 2. Enhancement Factor (E) as a function of Liquid-side Mass Transfer Coefficient ( $k_L^\circ$ ).**

Given these values, equation (4) yields  $J_{CO_2} \approx 1.3 \cdot 10^{-6} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ .