CAPTURING CARBON DIOXIDE DIRECTLY FROM THE ATMOSPHERE

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SUMMARY

The increasing concern over rising CO_2 levels in the atmosphere and their potential climate effects is fuelling research aimed at carbon management. One area of research focuses on capturing the CO_2 after combustion and sequestering it underground. Capture schemes would operate at the site of generation taking advantage of the elevated concentrations of CO_2 in the effluent. Here, however, we propose an indirect method of carbon capture that removes CO_2 from the atmosphere. This process combines existing technologies with recent technological innovations into a novel carbon capture concept termed air extraction. The process uses dissolved sodium hydroxide to remove the CO_2 from ambient air. The resultant sodium carbonate solution is causticized using calcium hydroxide to regenerate the sodium hydroxide solution and precipitate calcite. The calcite is then thermally decomposed to produce lime and CO_2. The lime is hydrated to complete the process. These latter stages are used routinely in the paper industry and the calcination of limestone is central to the cement industry. This paper reviews the process and highlights pertinent research to develop a likely cost-effective process. It is shown that the proposed process is well defined and technically feasible. The wide parameter space and potential for improvements suggest that further efficiency improvements are attainable. The most significant improvements will be derived from efficient heat management.

1 INTRODUCTION

Recent years have seen attention drawn to issues surrounding changes in the global climate induced by human activities. Concern over these potential changes has led to the formation of international agencies, such as the Intergovernmental Panel on Climate Change (IPCC), whose mission is to consider this problem. The IPCC has stated that carbon dioxide (CO_2) is the greenhouse gas contributing the largest portion of the anthropogenic increase in global radiative forcing, which the IPCC defines as an externally imposed perturbation in the radiative energy budget of the Earth's climate system. Anthropogenic CO_2 produces approximately 62% of the increase or 1.46 W/m^2 out of a total increase of 2.43 W/m^2 (Houghton and Ding, 2001). The increase in atmospheric CO_2 levels can be largely attributed to the combustion of fossil fuels, with a small contribution from cement production and land use changes. The total global emissions reached 6,611 million metric tons of carbon in 2000, which represents a 1.8% increase over 1999 (Marland, Boden and Andres, 2003). Given the world's economic dependence on fossil fuels and the expected increase in consumption, methods for mitigating the atmospheric release of CO_2 need to be developed.

The primary targets for mitigation are power plants as they produce large concentrated streams of CO_2 (Herzog and Drake, 1996). These sources account for about one third of the worldwide CO_2 emissions. Even after eliminating all emissions from power plants, the remaining two thirds would still be released to the atmosphere. Roughly half of all emissions arise from small distributed and often mobile sources. Mitigating their CO_2 impact on the atmosphere is more difficult. One approach is to provide fuels that are carbon free, which is the reason much emphasis is being placed on hydrogen as a transportation fuel. Here, we propose an alternative method for mitigating CO_2 emissions from sources other than power plants. We propose that CO_2 is removed directly from the atmosphere in a cost effective, industrial process hereafter referred to as air extraction.

Air extraction can be viewed as a variation of flue gas scrubbing where the fluid is at atmospheric temperature and pressure with a CO_2 concentration of 0.037%. The implementation of the process discussed here uses a sodium hydroxide (NaOH) based, alkaline liquid sorbent to remove the CO_2 from the ambient air by producing dissolved carbonate ions. In order to recover the sodium hydroxide, the resultant sodium carbonate (Na_2CO_3) solution is mixed with calcium hydroxide ($Ca(OH)_2$) to produce sodium hydroxide and calcium

with calcium hydroxide ($Ca(OH)_2$) to produce sodium hydroxide and calcium carbonate ($CaCO_3$) in a reaction known as causticizing. This reaction transfers the carbonate anion from the sodium to the calcium cation. The calcium carbonate precipitates, leaving behind a regenerated sodium hydroxide sorbent. The precipitate is dried, washed and thermally decomposed to produce lime (CaO). This step, known as calcination, is followed by hydrating the lime, known as slaking, which completes the process. The process of recycling of sodium hydroxide using calcium hydroxide has been in use in the pulp and paper industry since 1884, where it is known as the Kraft Process (Miner and Upton, 2002). This process also involves the calcination of limestone, which is at the heart of the cement manufacturing industry. In short, each unit process required is known to be technically feasible and the only remaining questions surround their efficiencies and costs.

This paper will present a review of the individual components comprising the air extraction process with a view to highlighting the potential benefits and concerns. The issues surrounding their integration into a functional air capture system will also be discussed. The layout of the paper will follow the path of the CO_2 molecule through the system. A simplified schematic of the process is shown in Figure 1.
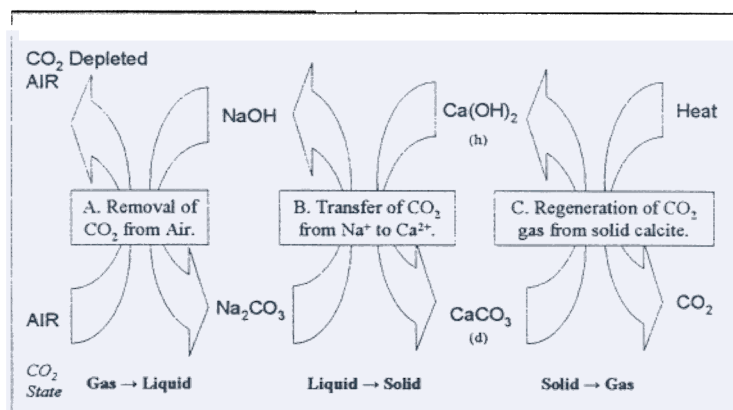

Figure 1 Overview of Air Extraction Process. Note that two reactions are not shown; drying (d), and hydrating (h).

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2 ALKALINE SODIUM SORBENTS

The removal of a gaseous component through contact with a liquid is known as wet scrubbing. Wet scrubbing can be divided into processes where there is a chemical reaction between the sorbate and the sorbent and where the sorbate is physically dissolved into the sorbent solution. For the air extraction process we propose an alkaline sodium solvent which reacts chemically with the entrained CO_2. The chemical reaction for this process is shown below as reaction (1).

$$2NaOH_{(aq)} + CO_{2(g)} \rightarrow Na_2CO_{3(aq)} + H_2O ; \tag{1}$$
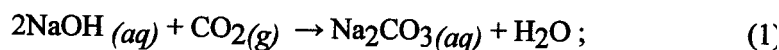
The aqueous carbonate reaction can be simplified by omitting the cation, resulting in the following ionic reaction.

$$2OH^-_{(aq)} + CO_{2(g)} \rightarrow CO_3^{2-}_{(aq)} + H_2O_{(l)} \tag{2}$$
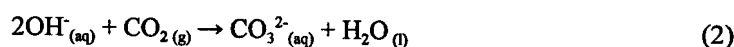
$$\Delta G^\circ = -56.1 \text{ kJ/mol } (\Delta H^\circ = -109.4 \text{ kJ/mol})$$

Note that the enthalpy and free energy of the reaction are for a nominal 1 molar solution. The thermodynamic data, given at 298K and a pressure of 1 bar, was obtained from the available literature (Lide, 2000). As a comparison, the free energy of mixing CO_2 with nitrogen and oxygen to form ambient air is given by

$$\Delta G = RT \ln (P_{atm}/P_{CO2}) \sim 20 \text{ kJ/mol} \tag{3}$$

Clearly, sodium hydroxide provides a sufficient driving force to effectively collect CO_2 from ambient air. Even though a lower binding energy might be desirable, the high binding energy of chemical sorbents proves useful in absorbing CO_2 from streams with low partial pressures of CO_2 (White, et al.,). As an alternative with a weaker binding energy, one may consider sodium or potassium carbonate buffer solutions as a sorbent. In this case the absorption can be described by:

$$CO_{2(g)} + CO_3^{2-} + H_2O_{(l)} \rightarrow 2 HCO_3^- \tag{4}$$
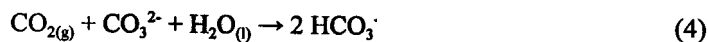
$$\Delta G^\circ = -14.3 \text{ kJ/mol} \quad (\Delta H^\circ = -27.6 \text{ kJ/mol})$$

Even in this case it is possible to muster a sufficient thermodynamic driving force to remove CO_2 from the air. For a two molar solution of bicarbonate

ions, the free energy of the reaction from ambient air is negative if the bicarbonate concentration stays below 0.15 molar. A similar result can be obtained by calculating the mass action equilibrium using empirical values for the equilibrium constants. Reaction (4) is effectively trimolecular and is the result of a sequence of reactions which have fast kinetics at high temperatures or very high carbonate to bi-carbonate ratios. Otherwise the process occurs in the diffusion regime, which is much slower (Astarita, 1967), making this reaction impractical for air extraction as it is kinetically limited.

In a recent review focused on flue gas, White et al. (2003) do not specifically discuss absorption on sodium hydroxide (NaOH), rather they consider aqueous solutions of sodium and potassium carbonate. These sorbents were compared to mono-ethanolamine (MEA), the industry standard, and it was concluded that MEA provides a substantially more cost-effective solution (Leci and Goldthorpe, 1997). At these higher CO_2 concentrations there would be no advantage in the higher binding energy of the hydroxide and the heat of this reaction is in any case irretrievably lost. An additional complication arises because the product carbonate cannot be decomposed with either heat or pressure. The resultant Na_2CO_3 must be efficiently decomposed chemically. We propose to accomplish the chemical decomposition using calcium hydroxide as an intermediary.

A sodium hydroxide solution provides a liquid sorbent that is more easily cycled through a piping system than a calcium hydroxide suspension. Its binding energy is strong enough and its reaction kinetics fast enough to obviate the need for heating, cooling or pressurizing the air. Because CO_2 is so dilute any such action would result in an excessive energy penalty. The hydroxide solution avoids all such complications. Since sodium hydroxide is cheaper than potassium hydroxide our starting point for the air extraction design will be based on sodium hydroxide.

2.1 Experimental Investigations into Sodium Hydroxide Sorbents

The absorption of CO_2 by NaOH solution was studied in 1943 by Tepe and Dodge (1943). Experiments were performed using a packed tower arrangement with the inlet gas having a CO_2 concentration of ~2%. Tepe and Dodge investigated the effects of NaOH concentration, Na_2CO_3 concentration, gas flow rate, solvent flow rate, and solvent temperature on the CO_2 uptake rate. The effects were quantified in terms of an over-all absorption rate coefficient. The results showed that the rate coefficient increased with increasing NaOH

concentration to a maximum normality of ~1.8 and then decreased. The rate coefficient decreased with increasing Na_2CO_3 concentration. The gas flow rate had no effect, while the rate coefficient increased with increasing solvent flow rates. The temperature of the solvent affected the rate coefficient significantly with the rate coefficient following the temperature of the solvent to the 6th power. The absence of sensitivity to gas flow rate and high sensitivity to temperature suggests that for these CO_2 concentrations, the reaction is limited by transport resistance in the liquid phase. More recent results on MEA solutions also show that at elevated CO_2 concentrations absorption is limited by resistance in the liquid phase (Aroonwilas et al., 2001).

Generally in wet scrubbing, one can break the transport resistance into two distinct components, the air side and liquid side resistance. The air side resistance is dominated by the diffusion barrier in the laminar boundary layer. Typically, such a boundary layer also exists on the liquid side. In the bulk fluid, dissolved CO_2 reacts with water, or hydroxide ions to form carbonate or bicarbonate ions. In contrast to the reactions of CO_2 with water, the reactions with hydroxide reactions are very fast and their reaction time can be ignored (Astarita, 1967). However, since diffusion coefficients of CO_2 in air are roughly four orders of magnitude larger than ionic diffusion coefficients in water, it is easy to become rate limited on the liquid side. The experiments of Tepe and Dodge suggest that the transport resistance is dominated by the liquid phase.

For a one molar carbonate ion concentration in the liquid, the concentration ratio between carbonate ions in the fluid and CO_2 molecules in the gas is 66,000: 1. It thus will take time to fill up a boundary layer on the liquid side. This suggests that at sufficiently low partial pressures of CO_2 the extraction process will be limited by air-side resistance.

The absorption of CO_2 from atmospheric air using an apparatus similar to that of Tepe and Dodge was studied by Spector and Dodge (Spector and Dodge, 1946). For ambient air, CO_2 absorption rates were proportional to G^α, where G is the air flow rate and the coefficient α varies from 0.35 at low flow rates to 0.15 at high flow rates.

This suggests that at low CO_2 concentrations, 0.031%, the liquid side resistance to transport ceases to be dominant. It is likely that in these experiments, fluid surface regeneration was sufficiently fast to prevent a built up of liquid-side flow resistance. The experiments did show that wet scrubbing using NaOH can effectively remove CO_2 from atmospheric air at a rate where the unavoidable air

side resistance to flow has become important. Spector and Dodge obtained approximately 90% removal for atmospheric concentration levels.

The advantage of using a strong hydroxide for CO_2 capture is a high load capacity and a fast reaction time. The results by Spector and Dodge suggest that a system can be built that will be limited by transport resistance in the air side of the air-liquid contact surface.

In a regime where the dominant transport resistance is on the air side, it is possible to estimate the size of the CO_2 extractor by the air drag the extractor causes on the flow. Apart from the pressure gradient driven momentum flow, momentum transfer to the wetted surface follows a similar transport equation as the CO_2 diffusion. As a consequence, a system that incurs a pressure drop roughly equal to ρv^2, which extracted virtually all of the initial momentum, will be able to extract a substantial fraction of the CO_2 from the flow. To set the scale of the operation, at 10m/s the air flow through an opening of $1m^2$ carries a CO_2 load that equals the CO_2 produced by generating 70 kW of heat from coal (Lackner, Grimes and Ziock, 1999). A 100 MW power plant operating at 33% efficiency would require $9,000m^2$ of wind cross section, if CO_2 collection efficiency would be about 50%.

3 CAUSTICIZATION

Causticization refers to the transformation of sodium carbonate into sodium hydroxide. It is generally performed by adding solid calcium hydroxide to the sodium carbonate solution. The solubility of calcium hydroxide is such that this forms an emulsion according to reaction (5).

$$Na_2CO_3\ _{(aq)} + Ca(OH)_2\ _{(s)} \rightarrow 2NaOH_{(aq)} + CaCO_3\ _{(s)} \tag{5}$$

This reaction can also be written in its ionic form as follows.

$$CO_3^{2-} + Ca(OH)_2\ _{(s)} \rightarrow 2OH^- + CaCO_3\ _{(s)} \tag{6}$$
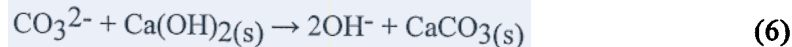
$$\Delta G^0 = -18.2\ kJ/mol \quad (\Delta H^0 = -5.3\ kJ/mol)$$

This process step regenerates the sodium sorbent. The CO_2 is removed as a solid through a filtration process. Zsako (1998) noted that one could also start with lime, which would slake immediately in the aqueous solution, but in air

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extraction, it is important recover the heat of the slaking reaction at elevated temperatures. Thus we have separated the slaking step from the causticization.

Experiments have shown that the causiticization rate increases with temperature (Dotson and Krishnagopalan, 1990). The initial sodium carbonate concentration for those experiments was ~2.0 mol/l and the samples were subjected to constant stirring. Reaction (5) eventually approaches equilibrium and causticizing efficiency is generally in the range of 80 to 90%. Causticizing efficiency refers to the amount of sodium carbonate converted to sodium hydroxide. Dotson (1990) determined that the rate constant for the reaction (5) increased by a factor 3 as the operating temperature was raised from 353 to 393K. The rate constant dropped when the feed solution contained sodium hydroxide. The experimental causticizing efficiency for pure sodium carbonate and a mixture of sodium hydroxide and sodium carbonate were ~94% and ~85% respectively.

The rate constant for the causticization is driven by the concentration of free Ca ions in solution. Highly alkaline solutions will limit the availability of dissolved Ca^{++} at any time and consequently reduce the rate of conversion. Elevated temperatures and active stirring reduce diffusional resistance and thus will increase the rate of reactions.

It was also noted that the concentrations of all the calcium species remain essentially constant throughout the reactions due to their low solubility. This suggests that the efficiency and rate constants may change if insufficient calcium is present. Dotson prevented this occurrence by using a 10% stoichiometric excess of lime. However, this excess results in solid calcium hydroxide being entrained with the filtrate. This would produce higher energy consumption in the lime kiln due to the dehydration reaction mentioned by Zsako (1998).

The concentrations of the various species, both sodium and calcium, have a profound effect on the quality of the resultant filtrate. Konno et al. observed that the solid phase of calcite is unstable in pure NaOH solution greater than 2 mol/l and easily converts to $Ca(OH)_2$ (Konno, Yasunori and Kitamura, 2002). These solids become stable in a 1 mol/l NaOH solution containing at least 0.02 mol/l Na_2CO_3. This latter solution mixture suggests that for an initial sorbent concentration of 1 mol/L, 96% of the hydroxide ions were converted to carbonate according to reaction (2). The presence of Na_2CO_3 also reduces the solubility of calcite. The solubility of $Ca(OH)_2$ is strongly dependent on the NaOH concentration and drops by a factor 4, to 5×10^{-4} mol/l, as the NaOH increases from 0 to 0.5 mol/l. Konno also observed the concentrations of Ca^{2+} and NaOH

during the reaction. As expected the Ca^{2+} concentration dropped and the NaOH concentration increased as the reaction progressed. The initial Ca^{2+} concentration was ~1 x 10^{-3} mol/l. Konno also noted that $Ca(OH)_2$ super saturation ratio is the driving force for nucleation. In effect, these processes balance the solubility of calcium hydroxide against the solubility of calcium carbonate. The values for the dissociation constants are available in the literature (Snoeyink and Jenkins, 1980).

$$[Ca^{++}][OH^-]^2 < K_{OH} = 10^{-1.49} \text{ mol}^3/l \tag{8}$$

$$[Ca^{++}][CO_3^{2-}] < K_{CO3} = 10^{-3.22} \text{ mol}^2/l \tag{9}$$

Given that the calcium concentration is the same in both (8) and (9), we can solve for the carbonate concentration as follows.

$$[CO_3^{2-}] = (K_{CO3}/K_{OH}) \times [OH^-]^2$$

Assuming a 1 molar sodium solution we can neglect the effect of calcium on the charge balance and the sodium concentration must therefore balance all the negative ions. If we further define the causticizing efficiency (ε) as the ratio of hydroxide ions over sodium ions we obtain the following relationship.

$$\varepsilon = \left(2 \frac{K_{CO3}}{K_{OH}} [OH^-] + \right)^{-1}$$

The stable solution suggested by Konno would contain approximately 1 mol per liter hydroxide ions. This would suggest a theoretical causticizing efficiency of 96%, which is slightly higher than the experimental value of Dotson et al. (1990). The difference is likely due to the omission of ionic activity in the calculations.

The experimental work discussed above provides a pathway for recovering sodium hydroxide from sodium carbonate. In the process, the carbon dioxide has been transferred into a solid form of calcium carbonate, which can be readily removed from the liquid and after washing and drying it can be thermally decomposed. The causticization takes place in an emulsion of calcium hydroxide. There are a number of options for the implementation, but this unit process is well established in the pulp and paper industry.

4 CALCINATION OF LIMESTONE

The final stage of the air extraction process is the recycling of the calcite precipitate. This is accomplished through thermal regeneration or calcination. Lime and limestone are among the oldest materials used by humanity with the first recorded use in the Egyptian pyramids. The first sound technical explanation of lime calcination came in the 18th century from the British chemist, Joseph Black (Boynton, 1966). There are three essential factors in the kinetics of dissociation; the dissociation temperature, the duration of calcination, and the CO_2 in the surrounding atmosphere. The reaction is shown below.

$$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}; \quad \Delta H^o = +179.2 \text{ kJ/mol} \qquad 12)$$
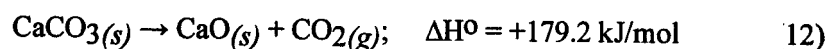
The first quantification of the thermal decomposition was performed in 1910 and the result was a decomposition temperature of 1171K in a 100% CO_2 atmosphere at atmospheric pressure (Johnston, 1910). Current practices use lime kilns to dissociate the calcite which vary greatly in their performance. The most important performance metric for air extraction is the thermal efficiency, which is the product of the theoretical heat requirement and the available oxide content divided by the total heat requirement. Boynton compares three hypothetical kilns and bases one on "the lowest fuel efficiency on record, that of the most advanced German mixed-feed kiln." This advanced kiln is reported to obtain a thermal efficiency of 85% for 93% available lime. The thermal efficiency refers to the proximity to the theoretical minimum heat requirement as defined by reaction (12) while the available lime refers to the amount of inert material present, in this case 7%. This translates into a total heat requirement of 3.03 MMBtu per ton of lime or 4.5 GJ per tonne of CO_2. This latter figure is lower than the 4.8 GJ per tonne of CO_2 used in a previous air extraction feasibility study (Zeman, 2003). The thermodynamic minimum heat requirement of 4.1 GJ/tonne CO_2 can be calculated from the enthalpy value in reaction (12).

The potential cost of air extraction will be dominated by this reaction and any improvement regarding the three kinetic factors listed above will directly affect the cost of the project. A lower dissociation temperature will require less heat input as will a shorter duration of calcination and a lower CO_2 content in the surroundings. Garcia-Labiano et al. found that calcination rate increased with temperature in a neutral environment and decreased with increasing CO_2 partial pressure and total pressure (Garcia-Libiano et al., 2002). Khinast et al. echoed

similar findings regarding the effects of CO_2 partial pressure but also found a decrease in reaction rates with increasing particle size (Khinast et al., 1996). The effect of steam on calcite decomposition was also investigated. It was found that steam enhanced the calcination rate and even compensated for the presence of CO_2 over the solid (Thompson and Wang, 1995). Thomson's experiments produced greater than 95% conversion after 40 minutes in an environment of 21% steam and 79% helium at a temperature of 753 K. The positive effects of steam on calcination may be synergistic with other advancements in improving the efficiency of calcination. In the case of lime mud calcination, Theliander proposed a novel steam drying system that reduces the overall system enthalpy by 33% (Theliander and Hanson, 1993). There are some novel designs for calcination units as well. The decomposition of limestone was tested in a solar reactor and achieved an average of ~50% conversion (Imhof, 1997).

5 AIR EXTRACTION AS CARBON CAPTURE

We are proposing to capture CO_2 directly from the atmosphere in a cost effective manner. As such, a brief comparison with the industry standards will provide a benchmark for future work. Sterically hindered amines (SHA) and MEA are considered potentially successful CO_2 capture technologies. They are regenerated using steam and their thermal energy requirements are 700 and 900 kcal/kg CO_2 for KS-2 and MEA, respectively (Mimura et al., 1997). These values can be converted to 2.9 and 3.8 GJ/ tonne CO_2. It should be noted that Mimura et al. captured 90% of the CO_2 generated by the power plants; the remainder would have to be mitigated by other means. An economic analysis of CO_2 capture using MEA obtained a cost of $50 per tonne of CO_2 avoided (Zappelli et al., 2003). Calcium based sorbents have also been investigated for use in CO_2 capture. The thermal requirements will follow the limits outlined above; however, the durability of the sorbent is also an important cost factor. This has been discussed for dry CO_2 cycles. Abanades summarized several studies of the carbonation/calcination cycle and found very good agreement (Abanades, 1998). Starting at around 80% conversion, performance rapidly dropped to less than 20% conversion at 14 cycles where it stabilized. These tests were conducted under different conditions than proposed for air extraction. Most importantly the air extraction process would hydrate or slake the resulting lime. Generally lime is regenerated in the hydration process, thus we do not expect a great reduction in capture efficiency from one cycle to the next. The process of hydration is

believed to proceed via the migration of water into the pores of the lime particle (Oates, 1998). The hydration reaction, shown below, then takes place.

$$CaO_{(s)} + H_2O_{(l)} \rightarrow Ca(OH)_{2(s)} \quad \Delta H^o = -64.5 \text{ kJ/mol} \tag{13}$$
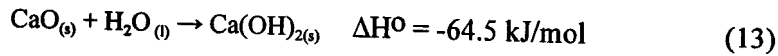
The hydration causes both expansion and the liberation of heat which causes the particle to split, exposing fresh surfaces and thereby reducing the effects of sintering. The inclusion of this reaction in the carbonation process will likely alter the performance and durability of the lime cycle, as will the lower temperatures of reaction. We believe that these differences preclude the use of durability data presented by Abanades as a deterrent from further study. Zsako (1998) stated that slaked lime undergoes dehydration at temperatures above ~700K under ambient conditions. This defines the range of possible operating temperatures for the hydration process. Hydration is highly exothermic and can provide useful heat energy if it is performed efficiently at high temperatures.

There are other methods for removing CO_2 from the atmosphere including physical absorption and refrigeration among others. Steinberg compared eight different methods of CO_2 removal and found alkaline wet scrubbing to be the least energy intensive (Steinberg and Dang, 1977). The estimated energy required to strip air of CO_2 was 0.4 kWh$_{(e)}$/lb methanol or 4.4 GJ/ tonne CO_2. The CO_2 was stripped using a 0.01 N K_2CO_3 solution and was desorbed by hydrogen, from electrolysis, and low pressure steam. It should be noted that this calculation did not include losses during the conversion of primary fuel to electricity.

The feasibility of air extraction will depend on the overall cost in comparison to alternate removal technologies. The cost per unit removal will further depend on the energy requirements, the durability of the sorbents, and costs external to the process. These external costs could include excessive water losses from the wet scrubbing. As this part of the process will be in contact with the open atmosphere, evaporation can be expected. This can be minimized by adjusting the sorbent concentration which varies the vapor pressure until it matches that of the ambient air. The thermophysical properties of sodium hydroxide solution are known for a wide range of concentrations (Olsson, Jernqvist and Aly, 1997). Other external costs will be delineated during bench and pilot scale demonstrations. The calcination reaction is likely the most energy intensive for the stated process. This highlights the need for efficient heat management within the system. Additionally, any significant lime degradation

will rapidly raise costs and CO_2 management issues. Lime make up will have to be generated through the calcination process, thereby releasing CO_2. This additional CO_2 will raise the cost of the process either through lowering the net amount avoided or increasing the total amount sequestered.

6 CONCLUSION

Our previous feasibility study mentioned earlier obtained a price range of ~$25-75 per tonne of CO_2 extracted (Zeman, 2003). The large range is due to the fluctuations in the price of natural gas and the uncertainty regarding the cost of solid oxide membranes. This range does match up with the quoted cost of MEA capture and does suggest further studies may provide a viable option for extracting CO_2 from the atmosphere. Air extraction is not necessarily more expensive than MEA capture in a flue stack. Even though the air contactors must be much larger than the equivalent contact surfaces in the flue stack, their contribution to the total cost may be very small. The recovery MEA sorbents requires similar amounts of energy, and because the air is clean and hydroxides are not subject to oxidative losses, the make-up costs are low in a hydroxide system. It is however clear, that the biggest challenge for air extraction will lie in the efficient management of heat and not in the design of the physical reactions.

The information highlighted in this paper maps out a large parameter space. We believe that such a broad discussion will prove useful in designing new implementations of processes that have been optimized in the past for entirely different goals. Our objective is quite different from that of the individual studies cited. The overall goal of the process is the maximize CO_2 capture while minimizing energy consumption. Variations in the operating conditions of each reaction should be investigated in order to quantify their effect on the entire process. For example, heating the fluid in the causticization reactor represents a compromise between increased energy consumption and longer reaction time. Sophisticated designs may maximize the amount of heat recaptured at elevated temperatures. For example, if the lime is hydrated using steam then the energy output of this reaction increases by the heat of condensation. This would be offset by steam generation elsewhere, but the higher quality heat obtained may be easier to harness. In the end, the minimum theoretical penalty for calcination is 4.1 GJ per tonne of CO_2 and the maximum energy recoverable from hydration is 1.5 GJ per tonne of CO_2. The resulting minimum net energy penalty is 2.6 GJ per tonne of CO_2, which is already lower than the practical energy cost of amine solutions.

Theoretical efficiencies may not be achievable in practice but they are an indication of the potential of the method.

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