AIChE WILEY InterScience® DISCOVER SOMETHING GREAT

R&D NOTE

Experimental Results for Capturing CO_2 from the Atmosphere

Frank Zeman
Earth and Environmental Engineering, Columbia University, 918 Mudd, MC 4711, New York, NY 10027

DOI 10.1002/aic.11452

Keywords: carbon dioxide, air capture, atmosphere, experiments results, transportation

Introduction

Methods for reducing anthropogenic carbon dioxide (CO_2) emissions are summarized in the IPCC Special Report on carbon capture and storage (CCS).[1] The report considers CO_2 emitters producing more than 0.1 Mega tonne (Mt) of CO_2 per year. The result is that 50% of current emissions will remain unabated even if conventional CCS is fully deployed. One proposed solution for the remainder is the capture of CO_2 directly from the atmosphere at a separate facility.

The concept of direct capture, known as air capture, was first considered in 1977 as part of a methanol synthesis process[2] and then revisited in the early 90s for renewable methanol production[3,4] using electrical energy to regenerate the CO_2 sorbent. An alternative process based on calcium oxide (lime) was later suggested.[5,6] The calcium concept was expanded to include the sodium hydroxide sorbent for CO_2 capture with subsequent causticization to produce calcite. Sodium was chosen as sorbent, as opposed to more reactive potassium, as it can be readily causticized using lime. The combined process was reviewed thermodynamically based on the available literature.[7] Others examined the energy and material balance of the sodium/calcium air capture system based on existing technologies.[8,9] These processes were compared to an optimized energy and material balance, which highlighted several important process parameters.[10] The work presented here includes partial results of an experimental investigation into the combined sodium/calcium capture process.[11] The thermodynamic basis for the sodium/calcium air capture process is provided as supplemental information.

Experimental Section

Experimental goals

The work presented here is a demonstration of the sodium/calcium air capture process, shown in Figure 1, with attention to a few specific parameters. The parameters of interest are CO_2 flux into solution, causticization efficiency, partial causticization, and filter cake moisture content. Each of these parameters plays an important role in the energy and material balance of the process. The CO_2 flux sets the size of the absorber, while the causticization efficiency measures the ability to regenerate sorbent. We expect causticization with mixed solutions of sodium carbonate and sodium hydroxide, and separately investigate partial causticization using fixed concentrations of NaOH and Na_2CO_3. The filter cake moisture content determines the amount of energy required for evaporation. The investigation was performed using a custom-built, bench-scale, air capture device. A detailed description of the experimental materials, plan, apparatus, and method are provided as supplemental information.

Results and Discussion

Capture of CO_2 from air

A summary of the CO_2 absorption data from the experimental program is presented graphically in Figure 2. The experiments are numbered in chronological order and were performed using the same [Na^+] absorbing solution. At the end of each absorption phase, the solution was causticized using lime to remove carbonate ions from solutions. The nonzero value at the start of the experiment is a reflection of insufficient lime added for causticization. The net effect was the migration of the zero value upwards, until extra lime was added after experiment IV. The zero value then migrated downwards, suggesting that causticizing with an excess of lime would maximize carbonate removal. The steady slopes

---

This article contains supplementary material available via the Internet at http://www.interscience.wiley.com/jpages/0001-1541/suppmat.

Correspondence concerning this article should be addressed to F. Zeman at fszl@columbia.edu.

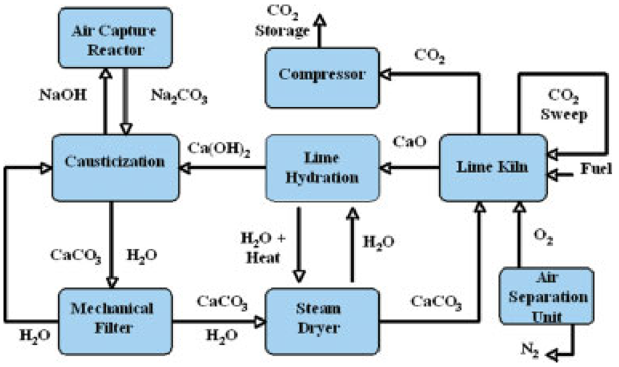

Figure 1. Overview of Na/Ca air capture process.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

suggest that absorption was not strongly linked to $[OH^-]$ or $[CO_3^{2-}]$ concentrations. Furthermore, no dramatic reduction in absorption was observed even at solution conversions over 50%.

Filter cake moisture content

Following the causticization reaction, the resulting suspension is separated using filtration, with vacuum pressures ranging from 80 to 90 kPa. The moisture content of the resultant filter cake is determined by drying the cake and measuring the mass loss. The precipitate sample was divided into four portions to accommodate existing filtration equipment. The data is presented in Figure 3 as the aggregate moisture content of the four portions with individual portion results represented by the error bars. The measurement error for each sample was negligible. The results show an average moisture content of 35%, with individual values ranging from 26% to 48%. It is noteworthy that higher ranges of values for the individual portions accompany higher moisture contents, which suggests segregation of the precipitate into coarse and fine portions.

The values are plotted against the dry sample mass that, given the fixed diameter of the filter, is a proxy for filter cake thickness. In this light, Figure 3 suggests a decreasing trend with reduced filter cake thickness that did not reach a minimum.

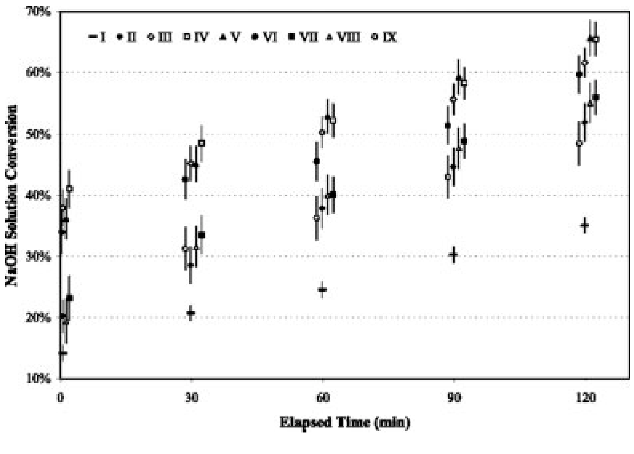

Figure 2. Summary of experimental results.

Note all measurements were taken on the half hour but are offset for presentation purposes.

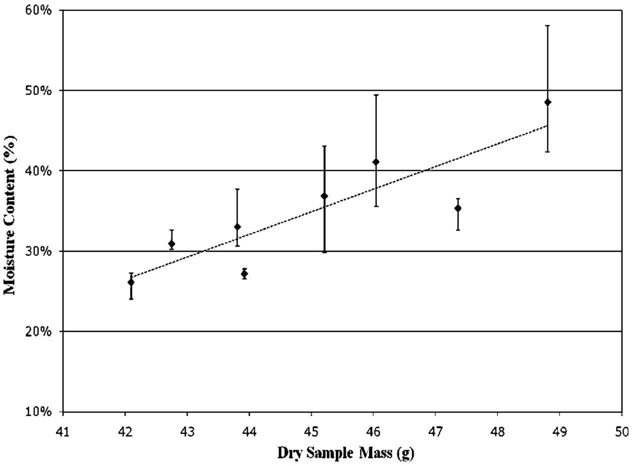

Figure 3. Correlation between filter loading and moisture content.

Note: data point represents aggregate moisture content of sample with range representing each portion.

Analysis using a scanning electron microscope showed a particle size ranging from 3 to 80 μm. The range observed contains particles larger than suggested by the literature (1–5 μm)[12] and indicates that seeding or interparticle forces are relevant.

CO_2 flux into solution

Data analysis contained in Table 1 established performance benchmarks that can be compared to previous work. The causticization efficiency is defined as the concentration ratio of hydroxide ions to the total sodium. It was measured at the start of the experiment. The trend shows that causticization efficiency decreases initially and then rises to above 80%. The increase coincided with the addition of extra lime to the cycle, although efficiencies near the theoretical limit[7] of 0.96 were not achieved.

The CO_2 flux is calculated by dividing the amount captured by the duration of the test, 120 min, and the available surface area of 4.12 m^2. Using the physical surface area rather than the active surface area will tend to underestimate the flux. The values ranged from 11.0 to 14.4 $\mu mol/m^2/s$ with an average flux of 12.3 $\mu mol/m^2/s$. The individual flux values were adjusted to reflect the varying CO_2 levels and [OH] concentrations. The adjustment converts all of the measured fluxes to those expected in a 375 ppm CO_2 atmosphere using a 1 M NaOH solution. An alkalinity of 1 mol/L is an upper limit, as higher values result in the precipitation of calcium hydroxide rather than calcite.[12] Equation 1 is taken from the theoretical derivation of Astarita,[13] which showed that the flux is proportional to the CO_2 concentration and square root of the hydroxide concentration. Astarita indicates that absorption of CO_2 into hydroxide solutions is a second-order reaction, although in the case of air capture, it is often considered pseudo-first order, given that the hydroxide ion concentration is four orders of magnitude greater than the CO_2 concentration (~1 mol/L vs. 15×10^{-6} mol/L).

$$\mathrm{Flux}_{\mathrm{corrected}} = \mathrm{Flux}_{\mathrm{measured}} \left(\frac{375}{P_{CO_2}} \right) \sqrt{\frac{1}{[\mathrm{OH}]_{\mathrm{avg}}}} \tag{1}$$

Table 1. Calculated Results from System Experiments

Experiment	[OH]/[Na]	Captured CO_2 (g)	Evaporation (g H_2O/g CO_2)	CO_2 Flux (μmol/m^2/s)	Flux Error (μmol/m^2/s)	Adj. Flux (μmol/m^2/s)
I	0.859	14.6	64	11.2	1.0	15.1
II	0.798	18.2	71	13.9	1.9	*
III	0.693	14.4	117	11.0	0.9	*
IV	0.650	14.7	83	11.2	0.9	20.7
V	0.639	16.3	95	12.5	1.2	20.4
VI	0.696	15.3	66	11.7	1.3	20.6
VII	0.824	18.8	124	14.4	1.6	20.3
VIII	0.865	17.7	92	13.6	2.3	19.2
IX	0.797	14.4	96	11.0	2.1	19.4

*Ambient CO_2 data unavailable.

The average adjusted flux is 19.4 μmol/m^2/s within a maxima of 20.7 and a minima of 15.0 μmol/m^2/s. Excluding experiment I, the adjusted fluxes are consistent, suggesting that absorption is not strongly related to [OH^-] or [CO_3^{2-}] concentrations. As a comparison, the highest flux measured by Spector and Dodge[14] is 10 μmol/m^2/s using ambient air at 315 ppm CO_2 (1946) and 2 M NaOH, which can be adjusted to 8.6 μmol/m^2/s. The improvement is attributable to the lower CO_2 removal in this work. Spector and Dodge removed over 90% of the CO_2 in the feed while we removed ~10%. Recalling that absorption is proportional to the CO_2 concentration in the gas phase, the expected improvement is the ratio of the average CO_2 levels in the absorption unit. Removing 10% of the CO_2 would result in an average CO_2 concentration of 356 ppm, which is 1.7 times larger than the adjusted average of 206 ppm from Spector and Dodge.

Evaporative water loss

The amount of water evaporation is determined by measuring the change in solution mass and then adding the amount of water added during the experiment and subtracting the mass of solute. We express this information as an evaporation ratio, which refers to the grams of water evaporated per gram of CO_2 captured. We compare this ratio to the relative humidity in the ambient air in Figure 4. The data shows a slight downward trend with increasing relative humidity. The average evaporative loss was 90 g H_2O for each gram of CO_2 captured. The calculation error ranged from 10 to 20%, and resulted from compounding experimental error that ranged from 2 to 5%.

Partial causticization

The ability to effectively causticize solutions only partially saturated with Na_2CO_3 is desirable in order to maintain high fluxes of CO_2 into solution.[10] A positive result would obviate the need for complete conversion of the sorbent solution to sodium carbonate. The investigation into partial causticization is summarized in Figure 5 with promising results. Figure 5 shows a series of lines, each representing a number of cycles. A cycle consisted of mixing the carbonate solution with the lime solids for 10 min in a stirred vessel. The solids were then separated using vacuum filtration, rinsed, and used in subsequent cycles. The analysis of the solids was done in a thermogravimetric analyzer.

The plots in Figure 5 show the conversion of the lime solids from calcium hydroxide to calcium carbonate. The temperature at which they decompose to lime, 4–500°C for calcium hydroxide and 6–800°C for calcium carbonate, identifies two compounds. After the first 10-min cycle, both solutions produce solids dominated by calcium hydroxide, as

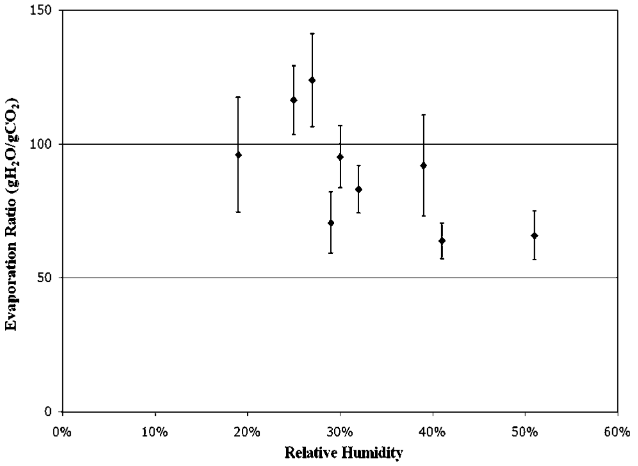

Figure 4. Measure of evaporative losses from air capture reactor.

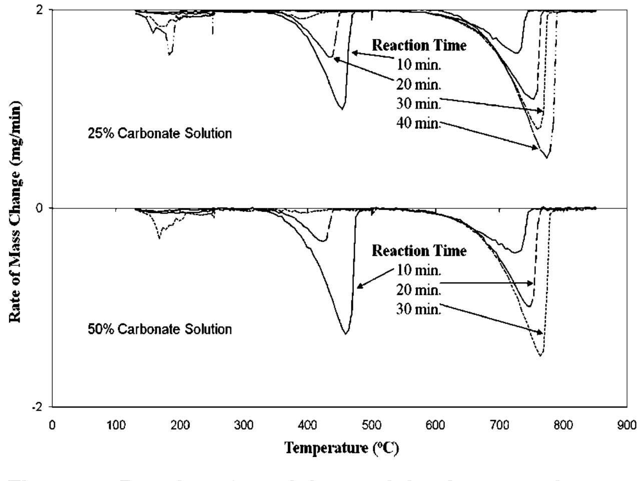

Figure 5. Results of partial causticization experiments.

shown in the solid line. The solids were completely converted to calcite after three cycles using the 50% solution and four cycles using the 25% solution. This suggests a total reaction time of less than 40 min for complete conversion of the calcium hydroxide to calcite. The low temperature ($<300^\circ$C) mass loss in Figure 5 is associated with hydrated states of calcite.

Conclusions

The experimental program successfully demonstrated components of an air capture process. The average adjusted CO_2 flux into solution was calculated to be 19.4 μmol/m^2/s for real world conditions. Further experimentation will focus on improving causticization methods, likely with an excess of lime, to ensure maximum hydroxide concentrations in the refreshed sorbent. The adjusted flux can be converted to a CO_2 capture rate of 960 g/m^3/h for the packing media used. The result is based on the conservative assumption that the entire available surface is absorbing CO_2.

The balance of the system portion confirmed important aspects of the process design. It is feasible to use conventional vacuum filtration techniques to produce filter cake with moisture contents less than 30%, significantly lower than the 50% value used by Keith et al.[9] and Baciocchi et al.[8] The amount of water lost to evaporation during these experiments averaged 90 g H_2O per g CO_2 and may be a significant economic and environmental penalty. Furthermore, the ability to causticize at ambient temperatures eliminates the thermal load required to heat the sorbent assumed by Keith et al.

Acknowledgments

This work has used the shared experimental facilities that are supported primarily by the Materials Research Science and Engineering Center (MRSEC) Program of the National Science Foundation (NSF) under Award Number DMR-0213574 and by the New York State Office of Science, Technology and Academic Research (NYSTAR).

Literature Cited

1. IPCC. *IPCC Special Report on Carbon Dioxide Capture and Storage*, In: Metz B, Davidson O, de Coninck H, Loos M, Meyer L, editors. Cambridge, UK: Cambridge University Press, 2005.
2. Steinberg M, Dang V-D. Production of synthetic methanol from air and water using controlled thermonuclear reactor power. I. Technology and energy requirement. *Energy Conv Manag*. 1977;17:97–112.
3. Bandi A, Specht M, Weimer T, Schaber K. CO_2 recycling for hydrogen storage and transportation—electrochemical CO_2 removal and fixation. *Energy Conv Manag*. 1995;36:899–902.
4. Stucki S, Schuler A, Constantinescu M. Coupled CO_2 recovery from the atmosphere and water electrolysis: feasibility of a new process for hydrogen storage. *Int J Hydrogen Energy*. 1995;20:653–663.
5. Lackner K, Grimes P, Ziock H J. In: *24th Annual Technical Conference on Coal Utilization*, Clearwater, FL, 1999.
6. Elliot S, Lackner KS, Ziock HJ, Dubey M, Hanson HP, Barr S, Ciszkowski NA, Blake DR. Compensation of atmospheric CO_2 buildup through engineered chemical sinkage. *Geophys Res Lett*. 2001;28:1235–1238.
7. Zeman FS, Lackner KS. Capturing carbon dioxide directly from the atmosphere. *World Resource Rev*. 2004;16:157–172.
8. Baciocchi R, Storti G, Mazzotti M. Process design and energy requirements for the capture of carbon dioxide from air. *Chem Eng Process*. 2006;45:1047–1058.
9. Keith DW, Ha-Duong M, Stolaroff J. Climate strategy with CO_2 capture from the air. *Clim Change*. 2006;74:17–45.
10. Zeman F. Energy and material balance of CO_2 capture from ambient air. *Environ Sci Technol*. 2007;41:7558–7563.
11. Zeman F. *Air Extraction: The Feasibility of Absorbing CO_2 directly from the Atomsphere*, **D.E.S.**, New York: Columbia University, 2006:167.
12. Konno H, Nanri Y, Kitamura M. Crystallization of aragonite in the causticizing reaction. *Powder Technol*. 2002;123:33–39.
13. Astarita G. *Mass Transfer with Chemical Reaction*. Amsterdam: Elsevier, 1967.
14. Spector NA, Dodge BF. Removal of carbon dioxide from atmospheric air. *Trans Am Inst Chem Engr*. 1946;42:827–848.

Manuscript received Oct. 26, 2007, and revision received Jan. 10, 2008.