Carbon Sequestration to Generate Calcium Carbonate: A Practical Approach to Sequester Residential CO2 Exhaust

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Abstract

The sequestration of carbon dioxide (CO2) from fossil fuel exhaust can reduce greenhouse gas emissions that contribute to global warming. Current methods of CO2 sequestration have multiple steps, are expensive, and potentially hazardous. In contrast, lime water sequesters CO2 to generate calcium carbonate (CaCO3) in a one-step process, producing a safe product that has many industrial applications. A laboratory model was designed to explore the potential of lime water to sequester CO2 from residential furnace exhaust. The quantity of CO2 sequestered and CaCO3 generated by lime water was theoretically calculated. Lime water, made from calcium hydroxide, was used to sequester CO2 from dry ice. The average amount of CaCO3 generated was 0.90 g/L lime water, which was statistically similar to the predicted value of 1.05 g/L lime water (p = 0.20). The experimental yield was 86%, and the quantity of CO2 sequestered was 0.40 g/L lime water. The volume of lime water required to sequester CO2 from the average American home furnace was determined, and a household sequestration apparatus was designed. This study supports the potential to utilize lime water as a novel approach to sequester CO2 from home furnace exhaust, and in turn aid in reversing global warming.

Introduction

Our culture is currently dependent on fossil fuel\(^1\), which generates significant quantities of greenhouse gasses upon combustion. Greenhouse gasses have been implicated to be responsible for contemporary global warming. Carbon dioxide (CO2) is the most prominent greenhouse gas generated by man, and the average American home produces 5,298 kg CO2 per year. Future generations may overcome the problems of fossil fuel combustion by implementing sustainable sources of energy. However, until that transition occurs, the detrimental effects of the production of greenhouse gasses needs to be addressed. Attempts to sequester CO2 have been met with difficulty, including the technological and economical problems of storing the sequestered CO2\(^2\). The use of a simple one-step approach to both simultaneously sequester and store CO2 exhaust would therefore be beneficial. In addition, if the stored CO2 could generate an environmentally safe and useful commodity, an economic incentive might help drive this process.

Carbon sequestration by bivalves has been a natural ecological process for ages. These organisms remove CO2 from seawater and use it to produce calcium carbonate (CaCO3) to establish a hard outer layer on their shells\(^1\). The sediment from these bivalves then forms limestone on the bottom of the ocean. Man, in turn, then harvests this limestone, and utilizes the CaCO3 as an ingredient for many industrial products, including paper, plastics and paint, as well as in the making of cement. The use of modern technology to simulate the ocean’s approach could therefore have a useful application for our current need to sequester and store greenhouses gasses. On a small scale, this process is currently being used to sequester CO2 from industrial exhaust\(^3\). Ingeniously, a cement company was established by collaborating with a desalination facility and an industrial plant, where industrial exhaust is percolated through ocean water to precipitate CaCO3 and generate calcium-free water. In addition to expanding this technology in the industrial arena, it could also be beneficial in the residential sector. For example, the exhaust from fossil fuels generated by home furnaces, cars, and lawn equipment could be sequestered and the resultant CaCO3 could then productively utilized by industry.

Lime water is created by adding calcium hydroxide (Ca(OH)\(_2\)) to water. When CO2 is percolated through the lime water, the CO2 interacts with the Ca(OH)\(_2\) to generate calcium carbonate (CaCO3) as per the chemical equation: Ca(OH)\(_2\) + CO\(_2\) -> H\(_2\)O + CaCO3. CaCO3 is poorly soluble and rapidly precipitates out of solution. The process is spontaneous, occurs in minutes, and the production of the limewater is inexpensive\(^4\). Therefore, the use of lime water could be a potentially useful resource to sequester CO2 to generate CaCO3.

In the context of this background information, the hypothesis of my experiment is: If carbon sequestration by lime water can be theoretically quantified, then a laboratory model can reproduce these predicted results and be applied to sequester CO2 from residential furnace exhaust. I therefore devised an experiment to attempt to address this.

Materials and Methods

**Set up of apparatus.** CO2 was generated by placing a 10 g piece of dry ice into 1L of room temperature distilled water within a 2 L Erlenmeyer flask. The CO2 gas then passed through plastic tubing whose end was place at the bottom of a 250 ml Erlenmeyer flask. The CO2 bubbled through the limewater for 2 minutes. The CaCO3 precipitated out of solution and was then weighed. Three parameters of this set-up were varied in an attempt to optimize the experiment: lime water preparation, use of controls, and method to remove the precipitated CaCO3.

**Lime water preparation:** Saturated lime water was made by dissolving 1.5g of Ca(OH)\(_2\) (Home Science Tools, CAS # 1305-62-0, lot # AD-10022-2, Billings, MT) into 1L distilled water at room temperature. At various time points (1 min, 40 min, or 24 hr) the lime water preparation was stopped, and excess precipitated Ca(OH)\(_2\) was removed by one of several methods (decanting, filtration through lab grade filter paper, or centrifugation) as per
the design of each experiment. *Experimental controls:* Each experiment was internally controlled by weighing each piece of filter paper before and after filtering to account for the variation in weight of each piece of filter paper. Where noted in the experimental design, a negative control was also employed where 200 ml of distilled water, rather than the experimental sample, was poured through filter paper. After drying, the change in weight of this negative control was subtracted from the weight of the experimental sample. This negative control was used to account for potential incomplete drying of the experimental sample, and to account for any change in weight of the filter paper by the experiment. *Removing precipitated CaCO3:* The precipitated CaCO3 was removed from the lime water by one of three methods: filtration with coffee filters, filtration with lab grade filter paper, or by centrifugation at 1000 rpm’s, (Beckman, model J6-HC), as per the design of each experiment. When filter paper was used, the filter paper was dried at room temperature for 12 hr prior to determination of yield.

**Determination of experiment duration:** The duration of the experiment was established by determining the time it took for all of the Ca(OH)2 in the lime water to be used to form CaCO3. This occurred when all of the lime water was transformed into water and CaCO3, as per the chemical reaction:

\[
\text{Ca(OH)}_2 + \text{CO}_2 \rightarrow \text{H}_2\text{O} + \text{CaCO}_3
\]

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\[
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\]

As the pH of lime water is pH 12.5, and the pH of water is pH 7, when the pH of the mixture reached pH 7, this indicated that all of the Ca(OH)2 was used up to form CaCO3. To determine this endpoint, the indicator bromothymol blue (Sigma, No. B-7271, lot # 51H3692, St. Louis, MO) was added to the lime water prior to bubbling through the CO2, as bromothymol blue is blue at pH 7.6 and yellow at a pH of 6.0. It was noted that the lime water turned yellow 1.5 minutes after the CO2 was bubbled through 200 ml of lime water. To assure that each subsequent experiment would run to completion, each experiment was stopped after a duration of 2 minutes. *Experimental Design* (Table 1): In four independent experiments, three parameters of the set-up were varied in an attempt to optimize the experiment: lime water preparation, use of controls, and method to remove the precipitated CaCO3. *Experiment #1:* Lime water preparation - 24 hr duration, then decanted; Controls - no negative controls; Removing the precipitated CaCO3 - filtration with coffee filters.

*Experiment #2:* Lime water preparation - 24 hr duration, then decanted; Controls - negative controls used; Removing the precipitated CaCO3 - filtration with lab grade filter paper.

*Experiment #3:* Lime water preparation - 24 hr duration, filtration with lab grade filter paper, then filtered again immediately prior to experimentation; Controls - negative controls used; Removing the precipitated CaCO3 - filtration with lab grade filter paper. *Experiment #4:* Lime water preparation - 1 min or 40 min duration, centrifugation immediately prior to experimentation; Controls - negative controls for filter paper not needed; Removing the precipitated CaCO3 - centrifugation.

<table>
<thead>
<tr>
<th>Experiment #</th>
<th>Lime water preparation(a)</th>
<th>Negative controls(c)</th>
<th>Removal of CaCO3(e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>24 hr, decanted</td>
<td>None</td>
<td>Coffee Filters</td>
</tr>
<tr>
<td>2</td>
<td>24 hr, decanted</td>
<td>Yes</td>
<td>Lab Grade Filter Paper</td>
</tr>
<tr>
<td>3</td>
<td>24 hr, filtered(b)</td>
<td>Yes</td>
<td>Lab Grade Filter Paper</td>
</tr>
<tr>
<td>4</td>
<td>1 min or 40 min centrifuged</td>
<td>Not needed(d)</td>
<td>Centrifugation</td>
</tr>
</tbody>
</table>

(a) **Lime water preparation:** At various time points (1 min, 40 min, or 24 hr) the lime water preparation was stopped, and excess precipitated Ca(OH)2 was removed by one of several methods (decanting, filtration through lab grade filter paper, or centrifugation).

(b) **Lime water was filtered again immediately prior to experimentation.**

(c) Change in weight of control filter paper after saturation with 200 ml distilled water then air dried at room temperature for 12 hours.

(d) **Control for filter paper not needed as no filter paper was used.**

(e) **CaCO3 was removed from the lime water by one of three methods:** filtration with coffee filters, filtration with lab grade filter paper, or by centrifugation.

### Results

**Generation of CaCO3 from lime water and CO2.**

Four independent experiments were repeated 5 times to generate CaCO3 from 200 ml limewater after CO2 from dry ice was percolated through the limewater. *Experiment #1* (Table 2): Limewater was prepared for 24 hr and then decanted. Coffee filters were used to remove the precipitated CaCO3, and the filter paper was weighed before each experiment. The mass of the precipitated CaCO3 was then calculated and reveals that an average of 0.12 g CaCO3 was precipitated from 200 ml lime water after 40 min. *Experiment #2* (Table 2): Limewater was prepared for 24 hr and then decanted. Coffee filters were used to remove the precipitated CaCO3. The filter paper was weighed before each experiment, and a negative control was used for each experiment to account for possible incomplete drying of the filter paper. The mass of the precipitated CaCO3 was then calculated. An average of 0.14 g CaCO3 was precipitated from 200 ml lime water (0.70 g CaCO3/L lime water). *Experiment #3* (Table 2): Lime water was prepared for 24 hr and then filtered with lab grade filter paper, and then filtered again immediately prior to experimentation. Lab grade filter paper was used to remove the precipitated CaCO3. The filter paper was weighed before each experiment, and a negative control was used for each experiment. The mass of the precipitated CaCO3 was then calculated. An average of 0.16 g CaCO3 was precipitated from 200 ml lime water (0.80 g CaCO3/L lime water). *Experiment #4* (Table 2): Limewater was prepared for 1 min or 40 min and then immediately centrifuged prior to use. Centrifugation was used to remove the precipitated CaCO3. An average of 0.12 g (1 min prep) and 0.18 g (40 min prep) CaCO3 was precipitated from 200 ml lime water (0.60 g and 0.90 g CaCO3/L lime water, respectively). Comparison of experimental results with predicted results is shown in Figure 1.
Discussion

Limewater sequesters CO2 to generate calcium CaCO3 in a one-step process, and the quantity of CO2 sequestered and CaCO3 generated per liter of lime water can be theoretically calculated. This study designed a laboratory model to match the theoretically predicted results, and attained a yield of 86% of the predicted results. The amount of limewater needed to sequester CO2 from home furnace was calculated and revealed the potential to apply this approach to sequester CO2 from home furnace exhaust.

Four independent experiments were performed to improve the yield and determine the best experimental design. The experimental design was improved upon from Experiment #1 to Experiment #4, as evidenced by increased yield (29% to 86%). When removing the precipitated CaCO3, it was evident that centrifugation (Exp. #4; 40 min) and lab grade filter paper (Exp. #2 and #3) gave the best results, but coffee filters (Exp. #1) were least effective. This most likely is because of increased porosity of the coffee filters as compared to the lab grade filter paper. Regarding the preparation of the lime water, removal of excess Ca(OH)2 by filtration or centrifugation rather than decanting would seem to be beneficial to avoid contaminating the CaCO3 collection, but this was not reflected in the data in Experiments #2 and #3. However, filtration or centrifugation of the limewater prior to use would avoid this variable. Negative controls were necessary when filter paper was used, as evidenced by the small but consistent weight change of these controls.

It is evident that the average yield of this laboratory model was at best 86% of the predicted value. This lower yield could have been due an insufficient duration of the experiment. For example, if the experiment was too short, not all of the CO2 would have been sequestered. If it was too long, the CaCO3 would dissolve in solution as calcium bicarbonate. Although Bromothymol blue identified a ballpark duration of the experiment, it would be helpful to use a pH meter, and stop the experiment exactly when the pH reaches 7. In addition, the range of the data for each experiment is fairly wide, particularly in Experiments #1-3. This may have been due to the use of filter paper to collect the precipitate, which required multiple measurements and multiple controls. This variable was avoided altogether by using centrifugation rather than by filtration (Exp. #4). Lastly, more experimental data points should improve the accuracy of the calculated averages.

Although lime water can be utilized to sequester CO2, it is important to note that CO2 is actually emitted when the Ca(OH)2 that is used to make the lime water is produced by the chemical industry. This is because Ca(OH)2 is commonly made by heating the CaCO3 present in limestone, a process which produces CO2 in addition to the Ca(OH)2. However, Ca(OH)2 can also be manufactured in the laboratory from a calcium salt and an alkali, rather than directly from limestone. As less CO2 is emitted into the atmosphere by this alternative process, using this source of Ca(OH)2 would make CO2 sequestration by lime water more efficient.

Table 2. Averaged results from each experiment.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Volume of Lime Water (ml)</th>
<th>Filter paper before experiment (g)</th>
<th>Change in Control filter paper (g)</th>
<th>CaCO3 Precipitate plus filter paper (g)</th>
<th>CaCO3 produced (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>200</td>
<td>1.006</td>
<td>n/a</td>
<td>1.068</td>
<td>0.062</td>
</tr>
<tr>
<td>2</td>
<td>200</td>
<td>1.568</td>
<td>0.02</td>
<td>1.73</td>
<td>0.14</td>
</tr>
<tr>
<td>3</td>
<td>200</td>
<td>1.55</td>
<td>0.034</td>
<td>1.744</td>
<td>0.16</td>
</tr>
</tbody>
</table>

Table 2. Averaged results from each experiment.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Time of Line Water Preparation (min)</th>
<th>Volume of Lime Water (ml)</th>
<th>Centrifuge tube before experiment (g)</th>
<th>CaCO3 Precipitate plus Centrifuge tube (g)</th>
<th>CaCO3 produced (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>1</td>
<td>200</td>
<td>50.85</td>
<td>50.97</td>
<td>0.12</td>
</tr>
<tr>
<td>4</td>
<td>40</td>
<td>200</td>
<td>50.83</td>
<td>51.006666667</td>
<td>0.18</td>
</tr>
</tbody>
</table>

Figure 1. Yield of the mean CaCO3 generated for each experiment as compared to the predicted results. (a) Percent yield of the predicted results. (b) Predicted results is 100% CaCO3 generated.
This approach of CO2 sequestration has been applied to the removal and storage of CO2 from industrial exhaust\(^1\). The study described herein explores the application of this approach to the sequestration of CO2 generated by residential fossil fuel combustion, specifically from the home furnace. It is therefore necessary to examine the economic and technical feasibility of this endeavor. The data in this study reveals that 0.90 g CaCO3 is generated from 1 liter of lime water (Exp. #4, 40 min). Therefore, 32.0 kg of CaCO3 would be generated by a residence each day from 35,500 L of lime water. This would translate into 11,680 kg CaCO3 each year. It could therefore be conceivable that such a company, possibly with government incentives, would pay for and establish the CO2 sequestration apparatus in each household, as well as set up curbside CaCO3 collection, similar to the collection of other recycled products (e.g., newspaper, glass, plastics).

The technical logistics for the sequestration apparatus in each household would also have to be practical. 35,500 L/day of limewater is too large of a volume to generate, store, and work with. However, if the limewater can be made more rapidly than every 24 hours, the water could be recycled and less water would be needed. Experiment #4 indicated that 40 min preparation is adequate (86% yield), and 1 min preparation is still effective (57% yield). For example, if limewater could be made every 5 min rather than every 24 hours, as these preliminary experiments suggest, this could reduce the volume of lime water by a factor of 1/288. A household would then only require 123 L of limewater each day, which is certainly more manageable.

A preliminary design for the household set-up is shown in Figure 2. The furnace exhaust would percolate through a 125 L tank of limewater to generate CaCO3 (CaCO3 Gen Tank) for a period of 5 minutes (125 L is roughly the size of a small bathtub). This tank would then be emptied, and the contents would pass through a continuous centrifuge where the precipitated CaCO3 would be removed. The supernatant would then be pumped to a second 125 L tank where it would be resaturated with Ca(OH)\(_2\) for a period of 5 minutes to generate lime water (LW Gen Tank). At this same time, limewater already saturated within the LW Gen tank will be pumped into the CaCO3 Gen Tank near the chimney to generate more CaCO3. In this way the two volumes of 125 L will be moved back and forth every 5 minutes between the two 125 L tanks. The centrifuge and LW Gen Tank can be located in the basement to allow for easier access by the homeowner, and the CaCO3 Gen Tank would be located high up in the chimney where the exhaust is at a cooler temperature. A pump would be required to circulate the limewater thought this system. The homeowner could take the CaCO3 outside for curbside collection. Although this is a rough scheme, and not detailed from an engineering perspective, it suggests the potential practicality of this set up.

![Figure 2. Design for household CO2 sequestration apparatus](image)

(a) CaCO3 generation tank (125 L).
(b) Lime water generation tank (125 L).
(c) Continuous centrifuge removes CaCO3.
(d) Exhaust redirected to the CaCO3 Gen Tank.
Future studies would be necessary to determine the minimal timeframe that limewater could be produced. It could also be explored if other salts, such as magnesium hydroxide, might be added to the limewater to sequester additional CO2, and be simultaneously precipitated with the CaCO3. Lastly, the engineering of the household apparatus needs to be explored in depth. A potential modification of the design might be the use calcium oxide (CaO) instead of Ca(OH)2 to make the lime water. The potential benefit is that the formation of limewater from CaO generates a large amount of heat which could be potentially harnessed for household heating, and to drive the motors for the centrifuge and the pump.

This study supports that limewater can be an innovative method to sequester CO2 that is safe, practical and economically advantageous, as CaCO3 is used for many industrial products (e.g., paint, paper, plastic, cement). In addition to sequestering CO2 from the home furnace, this approach for CO2 sequestration might also be applicable to other sources of residential CO2 exhaust, such as from automobiles and lawn equipment. Lastly, the application of this approach to industrial CO2 production could have an enormous impact on reducing large quantities of this detrimental greenhouse gas. The ultimate goal of this project is to use this approach of CO2 sequestration to help reverse global warming.

References

Acknowledgements
This research was conducted at the Teen Research and Education in Environmental Science (TREES) summer program at The University of Pennsylvania during the summer of 2010.