ABSTRACT

Issues associated with the use of Ba-based wet scrubbing systems for carbon capture from coal combustion-derived flue gas were investigated. Aqueous Ba(OH)$_2$ is an effective scrubbing medium for CO$_2$ at technologically reasonable liquid volumes and hence may potentially be useful for CCS applications. However, regeneration of the sorbent by thermal decomposition of the resulting carbonate requires high temperatures that impose an unacceptable energy cost associated with application of this approach.

Two approaches to overcoming this obstacle were investigated:

1. Destabilization of the BaCO$_3$ ionic lattice by inclusion of Mg and Ca
2. Decomposition of the carbonate in the presence of CO

Both approaches were experimentally tested in this project. Both pure and mixed phase Ba/Ca/Mg carbonates were prepared and their decomposition characteristics determined. It was found that the presence of Ca and Mg does result in increased decomposition of BaCO$_3$, as predicted; however, the magnitude of this effect is not sufficiently large to significantly reduce the energy requirements necessary for complete decomposition of the BaCO$_3$.

Addition of CO had no effect on the thermal decomposition properties of either BaCO$_3$ or mixed phase Ba/Ca/Mg carbonates. However, CO did very significantly lower the decomposition temperature of BaSO$_4$. This suggests that anecdotal reports of this effect are probably the result of use of Ba carbonate containing significant levels of BaSO$_4$ impurities. This result also suggests an alternative approach to the problem of Ba sorbent regeneration that may merit further exploration.
EXECUTIVE SUMMARY

The capture of CO₂ from flue gas generated by combustion-based coal fired power generation systems is likely to become essential for the continued viability of these systems in the future. Current leading technology for this purpose involves the use of amine-based scrubbing systems. These systems were originally developed for removal of CO₂ (and other “acid gases”) from natural gas streams, and application to coal flue gases has proven problematic, due to the presence of other oxides (e.g. SOₓ and NOₓ) and for other technological reasons.

The coal-fired utility industry has considerable experience with scrubbing of gases from flue gas. SOₓ removal by wet scrubbing is commonly practiced, especially by utilities utilizing relatively high sulfur coals, such as Illinois coals. The purpose of this exploratory project was to examine the feasibility of adaptation of this wet-scrubbing approach to the removal of CO₂ from flue gas.

The basic chemistry underpinning this approach is very well known. CO₂ will react with various alkaline earth metal hydroxides resulting in the formation of insoluble carbonates according to the general reaction:

\[
M(OH)_2 + CO_2 \rightarrow MCO_3 + H_2O
\]

Where \( M = Ca^{2+}, Mg^{2+}, or Ba^{2+} \), for example:

There are two fundamental obstacles to use of this approach for removal of CO₂ from flue gas:

1. Solubility limits of the metal hydroxides
2. Decomposition temperatures of the derived carbonates

The solubility limits of Mg(OH)₂, Ca(OH)₂ and Ba(OH)₂ are:

\[
K_{sp} \text{ Mg(OH)}_2 = 1.8*10^{-11} \text{ mol/L} \\
K_{sp} \text{ Ca(OH)}_2 = 5.5*10^{-6} \text{ mol/L} \\
K_{sp} \text{ Ba(OH)}_2 = 5*10^{-3} \text{ mol/L}
\]

The practical implication of these data is that removal of CO₂ from flue gas requires impractically large volumes of solution for Mg(OH)₂ or Ca(OH)₂. This is not the case for Ba(OH)₂ however, which, due to its much greater solubility has the potential to remove CO₂ from flue gases with technically feasible solution volumes (~ 40-50 L/m³ of flue gas at ~10% CO₂).

The draw back to this approach lies in the regeneration of the sorbent. In order to be technically feasible, the carbonate formed by reaction with CO₂ from the flue gas must be recycled to regenerate the sorbent according to the general equation.
MCO₃ → MO + CO₂
MO + H₂O → M(OH)₂

This can be accomplished thermally, however, the decomposition temperatures for MgCO₃, CaCO₃ and BaCO₃ are 434, 780 and ~1200 °C respectively. That is, decomposition of Mg carbonate occurs at readily accessible temperatures, but the corresponding hydroxide is too insoluble to be practical as a scrubbing agent, whereas Ba hydroxide is sufficiently soluble, but decomposition of the corresponding carbonate occurs at unacceptably high temperatures.

The primary purpose of this project was to explore potential means of lowering the decomposition temperature of BaCO₃ in order to reduce the energy penalty associated with use of Ba(OH)₂ based sorbents as carbon capture agents for flue gas clean up.

Two approaches to achieving this goal were investigated:

1. Destabilization of the BaCO₃ ionic lattice by inclusion of Mg and Ca
2. Decomposition of the carbonate in the presence of CO

The premise underlying the first approach is that the inclusion of “impurities” in the ionic lattice of any ionic solid introduces disorder into the lattice and, hence, lowers the overall lattice energy. Also, since CaCO₃ and MgCO₃ both decompose at lower temperatures than BaCO₃, decomposition of these within a predominantly BaCO₃ lattice may effectively catalyze decomposition of the BaCO₃, thereby lowering the overall energy required for decomposition.

The second approach is based on anecdotal reports, primarily from glass manufacturing, that report that addition of CO to glass firing kilns allows barium carbonate-based coloring agents to be used at temperatures accessible with typical small scale kilns. Both approaches were experimentally tested in this project. Both pure and mixed phase Ba/Ca/Mg carbonates were prepared and their decomposition characteristics determined. It was found that the presence of Ca and Mg does result in increased decomposition of BaCO₃ as predicted; however, the magnitude of this effect is not sufficiently large to significantly reduce the energy requirements necessary for complete decomposition of the BaCO₃.

Addition of CO had no effect on the thermal decomposition properties of either BaCO₃ or mixed phase Ba/Ca/Mg carbonates. However, CO did very significantly lower the decomposition temperature of BaSO₄. This suggests that anecdotal reports of this effect are probably the result of use of Ba carbonate containing significant levels of BaSO₄ impurities. This result also suggests an alternative approach to the problem of Ba sorbent regeneration that may merit further exploration.
OBJECTIVES

The overarching objective of this investigation was experimental verification of CO₂ capture using Barium-based wet scrubbing systems analogous to the wet scrubbing systems used for SOₓ capture. Specifically, this exploratory project was intended to accomplish two objectives:

1. Demonstration of the ability of Ba(OH)₂ to effectively capture CO₂ from gaseous streams.
2. Evaluation of decomposition of BaCO₃ to BaO, including investigation of the effect on decomposition temperature of the presence Ca and Mg in the solid carbonates and of CO in the decomposition atmosphere.

INTRODUCTION AND BACKGROUND

Carbon capture from flue gases generated by the conventional power plants is likely to become the key issue if coal is to become a near–emission free energy source. There is no proven technology for effective and environmentally acceptable scrubbing of CO₂ from flue gases. Currently, amine scrubbers are used commercially for capturing carbon dioxide. Alternatively, several sorbents have been reported in the literature. However, large scale commercial application of these sorbents have not been proven, primarily due to high cost of materials and large capital investments to replace amine scrubbing unit operations.

Based on thermodynamic and solubility considerations outlined in the initial proposal for this project, it was calculated that Ba(OH)₂ should be effective at capturing CO₂ in flue gas streams at technically reasonable concentrations and liquid washing volumes (~ 40 L of solution per m³ of flue gas). Conceptually, such a scrubber could be operated in a manner directly analogous to wet scrubbers operated for flue gas desulfurization (FGD). If correct, this approach could provide a technologically feasible alternative to amine scrubbers for capture of CO₂ from flue gases from coal fired power generation.

In chemical terms the process would operate as follows:

\[
\text{CO}_2 \text{ Capture} \quad \text{Sorbent Regeneration}
\]

\[
\text{Ba(OH)}_2 + \text{CO}_2 \rightarrow \text{BaCO}_3 + \text{H}_2\text{O} \quad \text{BaCO}_3 \rightarrow \text{BaO} + \text{CO}_2 \\
\text{BaO} + \text{H}_2\text{O} \rightarrow \text{Ba(OH)}_2
\]

The potential limitation of this approach lies in the high decomposition temperature of BaCO₃ to BaO, which must be accomplished in the regeneration step. If this temperature is unacceptably high, then the energy costs associated with regeneration of the BaO may be prohibitive.

The decomposition properties of pure BaCO₃ in an inert atmosphere are known. Under these condition BaCO₃ decomposes at temperatures >1200 °C, which is certainly
unacceptably high. However, two potential approaches to lowering this energy requirement were identified and were explored in this preliminary feasibility study:

1. Admixing of Ba with Ca and Mg carbonates. Both Mg and Ca are readily available and in many cases occur naturally within coal seams in the form of cleat filling minerals. The carbonates of both of these metals decompose at significantly lower temperatures than BaCO₃. It was hypothesized that solid solutions produced by co-precipitation of Ba/Ca/Mg(OH)₂ mixtures may be less stable than the pure compounds and hence may decompose more readily than (i.e. at lower temperatures) than the pure parent compounds, thereby reducing the energy penalty associated with regeneration of the solution used for CO₂ capture.

2. Decomposition in the presence of CO. Informal reports (primarily related to production of ceramics and glasses incorporating Ba salts for attainment of specific colorations) suggest that addition of CO to the decomposition atmosphere can significantly lower the decomposition temperature of BaCO₃. If correct, addition of CO to the regeneration atmosphere of the BaCO₃ produced by carbon capture could potentially significantly reduce energy costs associated with the proposed capture process and thereby enhance the overall process feasibility.

This project undertook preliminary studies to investigate both of these hypotheses.

EXPERIMENTAL PROCEDURES

Carbonate syntheses were accomplished by two strategies: co-precipitation by mixing of controlled ratios of (Ba(OH)₂), calcium hydroxide (Ca(OH)₂), and magnesium hydroxide (Mg(OH)₂), with excess Na₂CO₃; and precipitation by reaction of mixtures of Ba/Ca/Mg(OH)₂ with CO₂.

Saturated solutions of each of the hydroxides were prepared and pumped into the sodium carbonate solution using computer-controlled peristaltic pumps (Cole-Palmer Masterflex (L/S)/7550-50) were used to deliver the hydroxide solution(s) to the carbonate solution to form the desired product. Nitrogen (N₂) gas was blanketed over the hydroxide solution(s) to prevent them from reacting with CO₂ in the atmosphere.

Barium carbonate and barium mixed carbonates were also synthesized in the lab by using a bubbler apparatus. One gram of Ba(OH)₂ was dissolved in 400 mL of deionized water and poured into the bubbler apparatus. If reaction goes to completion, 1 g of Ba(OH)₂ should theoretically yield 1.15 g of BaCO₃. A constant, low volumetric flow of carbon dioxide was delivered to the bubbler. The starting pH of the hydroxide solution was approximately 12; pH was monitored throughout the reaction. The reaction was complete when the pH turned acidic. The reaction was stopped when pH decreased to below 6.5. Continued exposure to the CO₂ gas only acidified and dissolved the product. The carbonate product was filtered, dried, and weighed.
TGA analyses were carried out at the Coal Research Lab in Carterville, IL using a Perkin-Elmer/TGA7 Thermogravimetric analyzer. For each carbonate product, 6-15 mg was placed on the sample pan. Experiments were run using either N₂ or 5%CO in N₂ (45mL/min) as purge and reactant gas. Except where otherwise noted, all TGA measurements were performed with a 10°C/min heat up rate, starting at 50°C and ending at 1030°C (instrumental limit) final temperatures were held for 0-60 minutes depending on the requirements of the particular measurement.

RESULTS AND DISCUSSION

In order to be viable as a CO₂ capture technology, BaCO₃ precipitation must meet two primary requirements:

- Ba(OH)₂ must effectively capture CO₂ from gas streams containing CO₂.
- The resulting carbonate must be regenerable at reasonable conditions.

Both of these criteria were tested as part of this project.

Effective capture of CO₂ by Ba(OH)₂ was confirmed in this project by successful synthesis of BaCO₃ from Ba(OH)₂ by reaction with CO₂. Mixed Ba/Ca/Mg carbonates were also synthesized by this method. The efficiency of scrubbing of a gas stream containing CO₂ is highly dependent on flow rates, liquid volumes, and (especially) gas-liquid contact efficiency and is, therefore, highly dependent on contactor design. Optimization of contactor design was not an objective of this exploratory project, however, successful synthesis of these mixed-phase carbonates by reaction with CO₂ indicates that effective capture of CO₂ by this strategy is achievable.

The ultimate technical feasibility of this approach, however, is dependent not only on capture, but also on the regenerability of the sorbent by decomposition of the resulting BaCO₃. Evaluation of this aspect of this proposed process is described below.

Sorbent Regeneration

In order to test the second criteria, regeneration of BaO by thermal decomposition of Ba-containing carbonates, nineteen carbonate products over a range of barium/calcium/magnesium concentrations were synthesized for thermal analysis (see Table 1). These carbonates were intended to simulate the compositions of carbonates that may occur in actual Barium carbonate-based carbon capture systems, given that Ca and Mg from the coal would inevitably become co-mixed with the Ba during CO₂ capture. Furthermore, the decomposition temperatures of both MgCO₃ and CaCO₃ are significantly lower than that of BaCO₃ and it was, therefore, necessary to experimentally determine the decomposition properties of mixed phase carbonates in order to establish whether Ba/Ca/Mg carbonate solid solutions behaved as simple mixtures of the pure carbonates or whether the presence of mixed phased results in synergistic effects either lowering or raising decomposition temperatures.
The decomposition properties of all nineteen carbonates were tested using thermogravimetric analysis (TGA). Results from the pure carbonates, illustrated in Figure 1, show that MgCO$_3$ decomposes between 375°C and 480°C ($T_{\text{Max}} = 434^\circ\text{C}$), CaCO$_3$ decomposes between 630°C and 800°C ($T_{\text{Max}} = 780^\circ\text{C}$), and BaCO$_3$ has negligible decomposition over the temperature range achievable with existing TGA facilities (up to ~1000 °C).

Table 1

<table>
<thead>
<tr>
<th>BaCO$_3$ Barium/Calcium/Magnesium Carbonates</th>
<th>CaCO$_3$ Barium/Calcium Carbonates</th>
<th>MgCO$_3$ Barium/Magnesium Carbonates</th>
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<tbody>
<tr>
<td>$\text{Ba}<em>{0.880}\text{Ca}</em>{0.090}\text{Mg}_{0.030}\text{CO}_3$</td>
<td>$\text{Ba}<em>{0.900}\text{Ca}</em>{0.010}\text{CO}_3$</td>
<td>$\text{Ba}<em>{0.960}\text{Mg}</em>{0.010}\text{CO}_3$</td>
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<tr>
<td>$\text{Ba}<em>{0.900}\text{Ca}</em>{0.075}\text{Mg}_{0.025}\text{CO}_3$</td>
<td>$\text{Ba}<em>{0.920}\text{Ca}</em>{0.080}\text{CO}_3$</td>
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Figure 1. TGA results for decomposition of pure MgCO$_3$, CaCO$_3$ and BaCO$_3$.

Results from TGA analysis of Ba/Ca carbonates and Ba/Mg carbonates and Ba/Ca/Mg carbonates are illustrated in Figures 2, 3 and 4 respectively.
Figure 2. Thermal decomposition data for mixed Ba+Ca carbonates.

Figure 3. Thermal decomposition data for mixed Ba+Mg carbonates.
Figure 4. Thermal decomposition data for mixed Ba+Ca+Mg carbonates.

For the Ba/Ca carbonates, thermal decomposition data (Figure 2 and 4) indicate that the CaCO$_3$ phase fully decomposes from each product to CaO in the range of 600-800°C (consistent with the results for pure CaCO$_3$.) Likewise, the magnesium carbonate (Figure 3 and 4) fully decomposes from each product to MgO in the range of 350-450°C (consistent with the results for pure MgCO$_3$.) In both cases, thermal analysis indicates incomplete decomposition of the BaCO$_3$ phase. However, each case, the presence of Mg or Ca in the BaCO$_3$ matrix does (slightly) enhance the decomposition of BaCO$_3$. That is, the mass loss observed is greater than expected for the decomposition of the CaCO$_3$ or MgCO$_3$ phase alone. The magnitude of this effect varies from a few % to as much as 14% BaCO$_3$ decomposition (see Figures 5 and 6). This result is consistent with one of the original hypothesis upon which this project was premised, i.e. that mixed phase solid solutions of Ba/Mg/Ca carbonates would be less stable than the pure carbonates and hence would decompose at lower temperatures. However, the magnitude of the effect in and of itself is too small to adequately offset the energy penalty associated with regeneration of the Ba(OH)$_2$ sorbent.
Effect of CO on Sorbent Regeneration

As noted previously, anecdotal reports exist suggesting that addition of CO lowers the decomposition temperature of BaCO$_3$. If confirmed, this observation would have significant implications for the viability of Ba-based carbon capture technologies. Therefore, further TGA analyses were carried out in the present of CO to experimentally test these reports under controlled conditions. Multiple experimental measurements were taken, including decomposition of pure Barium, Calcium and Magnesium carbonates, and various mixed phase Ba/Ca carbonates Ba/Mg carbonates and Ba/Ca/Mg carbonates,
however, in all cases, the addition of CO to the decomposition atmosphere had no significant effect on the decomposition properties of the carbonates.

It is difficult, however, to simply dismiss the anecdotal reports of the effects of CO on the decomposition of Ba-containing products, since these are based on empirical observation, not theoretical postulates. Therefore, one additional set of experiments were undertaken using BaSO₄, rather than BaCO₃. The results of these analyses are illustrated in Figure 7.

![Figure 7. Thermal decomposition of BaSO₄ in the presence of CO, showing enhanced decomposition (negligible decomposition occurs over the accessible temperature range in the absence of CO).](image)

BaSO₄ typically undergoes thermal decomposition above 1600°C, well outside the temperature range achievable with the available TGA instrumentation. However, in the presence of CO, significant decomposition is observed at 900-1000°C. This represents an approximately 40% reduction in the energy demand required for decomposition of BaSO₄.

It is hypothesized that this effect is probably the result of the following reaction:

\[
\text{BaSO}_4 + \text{CO} \rightarrow \text{BaO} + \text{SO}_2 + \text{CO}_2
\]

This observation accounts for the reports of the effects of CO on the decomposition of BaCO₃ if one assumes that the carbonates tested were actually significantly contaminated with BaSO₄.

Since this reaction is beyond the scope of this exploratory project, no attempt has been made to optimize BaSO₄ decomposition conditions (particle size, flow rate CO.
CONCLUSIONS AND RECOMMENDATIONS

The high solubility of Ba(OH)$_2$ and its strong propensity to react with CO$_2$ make it potentially attractive as a carbon capture reagent for use in capture of CO$_2$ from flue gas streams from conventional coal fired power generation facilities. However, the high decomposition temperature of the resulting BaCO$_3$ is problematic, since the carbonate products must be decomposed to BaO during the recycling process and the high temperature required by this process imposes an unacceptable energy cost.

This project directly explored to approaches to overcoming this problem.

1. Decomposition of mixed phase Ba + Ca + Mg carbonates
2. Decomposition of Ba carbonate and mixed phase carbonates in the presence of CO

It was found that solid solutions of Ba Carbonate with Ca carbonate and Mg carbonate behave essentially as physical mixtures. Some evidence of minor synergistic effects resulting in lowering of the decomposition temperature of the Ba carbonate was observed, but this effect was not sufficiently large to overcome the large energy penalty associated with the use of Ba(OH)$_2$ for carbon capture.

The second approach, utilizing CO to enhance BaCO$_3$ was also unsuccessful. It was, however, observed that this effect is observed in the case of decomposition of BaSO$_4$. This suggests that it is likely that anecdotal reports describing this effect are actually the result of decomposition of BaSO$_4$ which can co-occur with BaCO$_3$ in some commercial preparations.

This observation suggests an alternative carbon capture strategy that may be viable that may circumvent the need for excessive regeneration temperatures associated with direct decomposition of BaCO$_3$. This alternative approach involves chemical decomposition of the Ba carbonate with sulfate and thermal regeneration of BaO from the sulfate phase rather than directly from the carbonate as illustrated schematically below:
This approach is more complex than the approach initially envisioned in this project, and the decomposition temperature of BaSO₄ in the presence of 5% CO (> 900°C) is still significantly high. However, this approach may achieve the original goal of a technically feasible wet scrubber system for CO₂ capture from flue gas from conventional coal fired power generation facilities, and may merit further exploratory investigation focused especially on optimization of BaSO₄ decomposition.
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This report was prepared by Dr Ken B. Anderson, Department of Geology, Southern Illinois University Carbondale, with support, in part, by grants made possible by the Illinois Department of Commerce and Economic Opportunity through the Office of Coal Development and the Illinois Clean Coal Institute. Neither Dr Ken B. Anderson Department of Geology, Southern Illinois University Carbondale, nor any of its subcontractors, nor the Illinois Department of Commerce and Economic Opportunity, Office of Coal Development, the Illinois Clean Coal Institute, nor any person acting on behalf of either:

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