Carbon Dioxide Capture from Flue Gas Using Dry Regenerable Sorbents

Final Report

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by
Thomas O. Nelson
David A. Green
Paul Box
Raghubir P. Gupta
Gunnar Henningsen
Brian S. Turk

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Submitted by:
RTI International\(^1\)
3040 Cornwallis Road
P.O. Box 12194
Research Triangle Park, NC 27709-2194

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\(^1\) RTI International is a trade name of Research Triangle Institute.
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<td>µm</td>
<td>micron</td>
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<tr>
<td>ACFM</td>
<td>actual cubic feet per minute</td>
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<td>APPCD</td>
<td>Air Pollution Prevention and Control Division</td>
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<td>BET</td>
<td>Brunauer Emmett Teller</td>
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<td>CANMET</td>
<td>CANMET Energy Technology Centre</td>
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<td>CEPCI</td>
<td>Chemical Engineering Plant Cost Index</td>
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<td>CO₂</td>
<td>carbon dioxide</td>
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<td>COE</td>
<td>cost of electricity</td>
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<td>carbonyl sulfide</td>
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<td>Davison Index</td>
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<td>DSCM</td>
<td>cubic meter of dry standard</td>
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</tr>
<tr>
<td>IFRF</td>
<td>International Flame Research Foundation</td>
</tr>
<tr>
<td>IGCC</td>
<td>integrated gasification combined cycle</td>
</tr>
<tr>
<td>I/O</td>
<td>input/output</td>
</tr>
<tr>
<td>kWh</td>
<td>kilowatt hour</td>
</tr>
<tr>
<td>Li₂CO₃</td>
<td>lithium carbonate</td>
</tr>
<tr>
<td>Li₂SiO₃</td>
<td>lithium meta-silicate</td>
</tr>
<tr>
<td>Li₄SiO₄</td>
<td>lithium ortho-silicate</td>
</tr>
<tr>
<td>LSU</td>
<td>Louisiana State University</td>
</tr>
<tr>
<td>MEA</td>
<td>monoethanolamine</td>
</tr>
<tr>
<td>MFCs</td>
<td>mass flow controllers</td>
</tr>
<tr>
<td>min</td>
<td>minute</td>
</tr>
<tr>
<td>MPCRIF</td>
<td>Multipollutant Control Research Facility</td>
</tr>
<tr>
<td>MWₑ</td>
<td>megawatt electrical</td>
</tr>
<tr>
<td>MWh</td>
<td>megawatt hour</td>
</tr>
<tr>
<td>Na₂CO₃</td>
<td>sodium carbonate</td>
</tr>
<tr>
<td>Na₂CO₃•3NaHCO₃</td>
<td>Wegscheider’s salt</td>
</tr>
<tr>
<td>Na₂CO₃•NaHCO₃•2H₂O</td>
<td>sodium sesquicarbonate</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>-------------</td>
</tr>
<tr>
<td>NaHCO₃</td>
<td>sodium bicarbonate</td>
</tr>
<tr>
<td>NaHCO₃•2H₂O</td>
<td>sodium bicarbonate hydrate</td>
</tr>
<tr>
<td>NETL</td>
<td>National Energy Technology Laboratory</td>
</tr>
<tr>
<td>O₂</td>
<td>oxygen</td>
</tr>
<tr>
<td>PC</td>
<td>pulverized coal</td>
</tr>
<tr>
<td>PID</td>
<td>proportional/integral/derivative</td>
</tr>
<tr>
<td>ppm</td>
<td>parts per million</td>
</tr>
<tr>
<td>PRB</td>
<td>Powder River Basin</td>
</tr>
<tr>
<td>SCADA</td>
<td>supervisory control and data acquisition</td>
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<tr>
<td>SCFH</td>
<td>standard cubic feet per hour</td>
</tr>
<tr>
<td>SCFM</td>
<td>standard cubic feet per minute</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscope</td>
</tr>
<tr>
<td>SLPM</td>
<td>standard liters per minute</td>
</tr>
<tr>
<td>SCR</td>
<td>selective catalytic reduction</td>
</tr>
<tr>
<td>SO₂</td>
<td>sulfur dioxide</td>
</tr>
<tr>
<td>TCR</td>
<td>total capital requirement</td>
</tr>
<tr>
<td>TGA</td>
<td>thermogravimetric analysis</td>
</tr>
<tr>
<td>TPD</td>
<td>thermally programmed desorption</td>
</tr>
<tr>
<td>VFD</td>
<td>variable frequency drive</td>
</tr>
<tr>
<td>WFGD</td>
<td>wet flue gas desulfurization</td>
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</tbody>
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Abstract

Regenerable sorbents based on sodium carbonate (Na$_2$CO$_3$) can be used to separate carbon dioxide (CO$_2$) from coal-fired power plant flue gas. Upon thermal regeneration and condensation of water vapor, CO$_2$ is released in a concentrated form that is suitable for reuse or sequestration. During the research project described in this report, the technical feasibility and economic viability of a thermal-swing CO$_2$ separation process based on dry, regenerable, carbonate sorbents was confirmed. This process was designated as RTI’s Dry Carbonate Process. RTI tested the Dry Carbonate Process through various research phases including thermogravimetric analysis (TGA); bench-scale fixed-bed, bench-scale fluidized-bed, bench-scale co-current downflow reactor testing; pilot-scale entrained-bed testing; and bench-scale demonstration testing with actual coal-fired flue gas. All phases of testing showed the feasibility of the process to capture greater than 90% of the CO$_2$ present in coal-fired flue gas. Attrition-resistant sorbents were developed, and these sorbents were found to retain their CO$_2$ removal activity through multiple cycles of adsorption and regeneration.

The sodium carbonate–based sorbents developed by RTI react with CO$_2$ and water vapor at temperatures below 80°C to form sodium bicarbonate (NaHCO$_3$) and/or Wegscheider’s salt. This reaction is reversed at temperatures greater than 120°C to release an equimolar mixture of CO$_2$ and water vapor. After condensation of the water, a pure CO$_2$ stream can be obtained. TGA testing showed that the Na$_2$CO$_3$ sorbents react irreversibly with sulfur dioxide (SO$_2$) and hydrogen chloride (HCl) (at the operating conditions for this process). Trace levels of these contaminants are expected to be present in desulfurized flue gas. The sorbents did not collect detectable quantities of mercury (Hg).

A process was designed for the Na$_2$CO$_3$-based sorbent that includes a co-current downflow reactor system for adsorption of CO$_2$ and a steam-heated, hollow-screw conveyor system for regeneration of the sorbent and release of a concentrated CO$_2$ gas stream. An economic analysis of this process (based on the U.S. Department of Energy’s National Energy Technology Laboratory’s [DOE/NETL’s] “Carbon Capture and Sequestration Systems Analysis Guidelines”) was carried out.

RTI’s economic analyses indicate that installation of the Dry Carbonate Process in a 500 MW$_e$ (nominal) power plant could achieve 90% CO$_2$ removal with an incremental capital cost of about $69 million and an increase in the cost of electricity (COE) of about 1.95 cents per kWh. This represents an increase of roughly 35.4% in the estimated COE – which compares very favorable versus MEA’s COE increase of 58%. Both the incremental capital cost and the incremental COE were projected to be less than the comparable costs for an equally efficient CO$_2$ removal system based on monoethanolamine (MEA).
1.0 Executive Summary

The primary objective of this project is to develop a commercially feasible process to separate carbon dioxide (CO₂) as an essentially pure stream from a fossil fuel combustion system using a regenerable sorbent. The sorbents being investigated for this effort are based on alkali carbonates, particularly sodium carbonate (Na₂CO₃). The carbonate in these sorbents is converted to bicarbonate or an intermediate salt (Wegscheider’s salt) through reaction with CO₂ and water vapor. The sorbent is regenerated back to its carbonate form when heated, producing a nearly pure CO₂ stream after condensation of water vapor. The process designed around these reactions was named as RTI’s Dry Carbonate Process.

Pursuant of a commercial Dry Carbonate Process technology, RTI’s research focused in two main areas: sorbent development and process development. In the sorbent development area, pure forms of sodium carbonate (e.g., different grades of sodium bicarbonate, soda ash, trona) were tested due to their attractiveness as abundant and cheap materials. Supported sorbents (Na₂CO₃ on an inert catalyst support material) and various methods of preparation were attempted in order to capitalize on the higher surface area and physical strength associated with these materials. Supported sorbents proved to be the most attractive option for the Dry Carbonate Process due to requirements for high physical strength and reactivity. RTI’s research focused on developing a supported carbonate sorbent optimized for attrition-resistance and reactivity (two properties of great importance for entrained-bed operation). RTI studied the advantages and disadvantages of using different support materials, different preparation methods, different ratios of carbonate and support, different carbonate precursors, and pH adjustment during preparation. Screening tests were used as a way of eliminating any of the sorbents that did not meet the desired reactivity, attrition-resistance, surface area, or particle size distribution. The most promising sorbents were then subjected to fluidized-bed testing in simulated flue gas in order to get a more realistic measure of sorbent performance. These efforts have led RTI to the development of a sorbent which is suitable for commercial entrained-bed reactor operation. Manufacture of RTI’s sorbent material has been carried out by Süd-Chemie, Inc. (SCI) in commercial manufacturing equipment. Sorbent preparations carried out by SCI have proven the reproducibility of sorbent properties and chemistry in commercial equipment. SCI manufactured roughly 500 lbs of RTI’s supported sorbent materials during the project timeframe. Additional sorbent development observations and achievements are listed here:

Sorbent Development Observations & Achievements

- Low cost sorbent material identified for CO₂ capture applications
- CO₂ capture activity shown to be stable over multiple cycles
- Reactions with SO₂ & HCl evaluated and quantified
- Supported sorbent shows significant improvement in reactivity
- Attrition-resistance of supported sorbent is ideal for fluidized/circulating reactors
- Optimal support and preparation method identified
- Supported sorbent manufactured in commercial equipment by catalyst manufacturer

Process development activities focused on solving the many unique challenges associated with post-combustion CO₂ capture in general, and CO₂ capture using sodium carbonate. Process development observations and achievements are summarized here:
Process Development Observations & Achievements

- Operating temperature ranges identified
- Regeneration in pure CO₂ demonstrated
- >90% CO₂ capture capacity demonstrated in fixed-bed and fluidized-bed studies
- Rapid initial CO₂ removal observed in fluidized-bed tests
- Temperature rise during adsorption caused decline in removal rates (in both fixed- and fluidized-bed studies)
- Better temperature control was observed in entrained-bed reactor studies
- Developed novel process design based on entrained adsorption / indirect heating for sorbent regeneration
- Bench-scale Dry Carbonate Process demo unit built at RTI
- >90% CO₂ capture capacity proven using bench-scale unit and actual coal-fired flue gas and simulated flue gas

Initial research utilized thermogravimetric analysis (TGA) to gain a full understanding of the chemistry involved in the process. These analyses proved the feasibility of the Dry Carbonate Process to remove CO₂ and to reliably cycle between sorption and regeneration under realistic flue gas conditions. Building on the TGA results, RTI designed and carried out several fixed-bed and fluidized-bed tests under simulated flue gas conditions for both the adsorption and regeneration reactions. Laboratory fluidized-bed testing of supported sorbents composed of 10 - 15 wt% Na₂CO₃ on a ceramic support showed that these materials can achieve significant CO₂ removal until saturation capacity is reached. These sorbents release essentially all of the CO₂ adsorbed when heated to 150° to 180°C. Despite encouraging results from these tests, the collected data did show that fixed-bed and dense phase fluidized-bed systems are not optimal reactor schemes for the Dry Carbonate Process. The poor heat transfer and poor heat removal inherent to these systems causes the reaction rates to slow and eventually cease. RTI considered using an entrained-bed type system to distribute and remove heat more effectively as well as carry out adsorption and regeneration in a continuous fashion.

Testing of an RTI’s supported sorbent in a pilot-scale entrained-bed reactor system was successful in that the sorbent was demonstrated to retain its activity over multiple cycles in simulated flue gas. Regeneration of the sorbent was conducted in fluidized-bed mode in nitrogen. Essentially, complete thermal regeneration was successfully demonstrated. The sorbent was shown to be mechanically stable by conducting and comparing particle size distribution determinations on samples of the sorbent after each test cycle.

Utilizing data collected during pilot-scale entrained-bed reactor testing, RTI developed a novel contacting scheme to employ supported Na₂CO₃ sorbents for removal of CO₂ from simulated flue gas. A sorbent composed of 15 wt% Na₂CO₃ on an inert support was used in a co-current downflow reactor to remove >90% of the CO₂ from a simulated flue-gas mixture containing 15 vol% CO₂. A bench-scale process prototype composed of a downflow reactor coupled with two screw conveyors (one steam heated for sorbent regeneration and the other water cooled for sorbent cooling) was designed and successfully operated at RTI using simulated flue gas. RTI moved this bench-scale Dry Carbonate Prototype Unit to the U.S. Environmental Protection Agency’s Multi-Pollutant Control Combustion Research Facility (MPCRF) in Research Triangle Park, North Carolina to demonstrated the technology using actual coal-derived flue gas. EPA’s 4 million Btu/hr multi-fuel (coal, gas, oil) facility can burn roughly 330 lbs/hr of coal and 120 m³/hr of natural gas (flue gas flow is roughly 1,000 standard cubic feet per minute).

The Dry Carbonate prototype was tested with actual natural gas–derived and coal-derived flue gases. The system demonstrated >90% capture of the CO₂ from both types of flue gases as well as complete regeneration of the sorbent material. The bench-scale system was operated with natural gas–
derived and coal-derived flue gas for roughly 130 and 105 hours, respectively. Several observations and achievements from this testing are summarized here:

### EPA Field Test Observations & Achievements

- >90% CO₂ capture achieved from both coal and natural gas flue gas
- Over 235 hours of fossil fuel-fired testing achieved
- Prototype system is capable of sustained CO₂ capture over several hours
- Testing with actual flue gas showed little difference in CO₂ capture performance compared to simulated flue gas testing
- No adverse performance effects observed due to contaminants in flue gas.
- Sorbent proved to be stable and only showed minor signs of physical wear.
- Regeneration temperatures > 120°C are ideal for full sorbent regeneration
- CO₂ capture performance improves with more complete sorbent regeneration
- Amount of steam delivered is important criteria to achieve target regeneration
- Capture performance improves with longer adsorption residence time
- Deeper cooling of sorbent improves CO₂ removal performance
- Continued development of sorbent – to increase CO₂ working capacity – is required

Laboratory and bench-scale testing confirmed that the Na₂CO₃-based sorbents would also react with sulfur dioxide (SO₂) and hydrogen chloride (HCl) which are typical contaminants present in coal-derived flue gas. The reactions of Na₂CO₃ with SO₂ and HCl are essentially irreversible at the desired process conditions of the Dry Carbonate Process - forming sodium sulfate (Na₂SO₄) and sodium chloride (NaCl) respectively. The design of RTI’s Dry Carbonate Process takes into account the need to replenish sorbent due to the loss of active material reacting with SO₂ and HCl and the loss of sorbent due to physical attrition. It should be noted, however, that in post- wet flue gas desulfurization flue gas SO₂ and HCl are present at much lower concentrations than CO₂ – less than 20 ppm for SO₂ and 1 ppm for HCl. For a commercial-scale Dry Carbonate Process, installed at a 500 MWₑ (nominal) power plant, the calculated rate of Na₂CO₃ loss due to reaction with contaminants is only slightly above the rate of sorbent make-up required due to physical attrition – 471 and 418 lbs/hr respectively. At steady-state. The Dry Carbonate Process operates with a fresh sorbent make-up rate that is nearly the same as Na₂CO₃ loss due to reaction with contaminants. Therefore, for design and analysis purposes, it was assumed that Na₂SO₄ and NaCl are evenly distributed within the sorbent bed at low, steady-state operating concentrations. It is not expected that these compounds will accumulate much over time. The rate of sorbent replenishment in the system is assumed to be the higher of the two values and do not need to be added together due to the tolerance for a low steady-state concentration of contaminants. RTI’s research shows little or no impact on CO₂ capture activity due to the presence of small concentrations of Na₂SO₄ and NaCl.

In regards to other flue gas contaminants, RTI’s sorbent adsorbed little or no mercury (Hg) vapor at the conditions of interest. It is expected that Hg vapor will have little impact on sorbent replenishment needs for the Dry Carbonate Process. Overall, it was calculated that a commercial-scale Dry Carbonate Process (at a 500 MWₑ nominal power plant) will require an initial sorbent loading of roughly 387 tons and the make-up rate of fresh sorbent will be on the order of 1/5 ton per hour. Thus the sorbent bed will be fully replenished every 3 – 6 months depending on the capacity factor of a given power plant.

Based on the experimental data gathered in this project, a conceptual process design of a commercial system was developed for 90% CO₂ removal from a coal-fired PC plant. Using this conceptual design, a comparative economic analysis of the Dry Carbonate Process and the
monoethanolamine (MEA) CO₂ removal process was carried out. When applied to a 500 MWₑ (nominal) coal-fired power plant, the Dry Carbonate Process was found to have lower incremental capital costs than an MEA system ($69 million vs. $114 million) and was estimated to result in a lower increase of a power plant’s cost of electricity (COE) (1.95 cents/kWh vs. 3.2 cents/kWh). The estimated impact of implementing the Dry Carbonate Process at a power plant was roughly a 35.4% increase in the COE. This estimated cost increase is slightly higher than DOE targets of limiting COE increase to 35%, but the Dry Carbonate Process is significantly lower in cost and more energy efficient than conventional MEA technology (DOE cost targets for CO₂ capture technologies are provided in the DOE National Energy Technology Laboratory’s (DOE/NETL’s) Carbon Sequestration Technology Roadmap and Program Plan – 2007 (http://www.netl.doe.gov/publications/carbon_seq/project%20portfolio/2007/2007Roadmap.pdf)). An overall comparison of the economics of a power plant with no CO₂ capture (Case 7C), one with MEA CO₂ capture installed (Case 7A), and one with Dry Carbonate CO₂ capture is shown here:

<table>
<thead>
<tr>
<th>Summary</th>
<th>No CO₂ Capture (Case 7C)</th>
<th>With CO₂ Capture (Case 7A)</th>
<th>With CO₂ Capture (Dry Carbonate)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Levelized Capital Charge Factor (%)</td>
<td>14%</td>
<td>14%</td>
<td>14%</td>
</tr>
<tr>
<td>Capacity Factor (%)</td>
<td>65%</td>
<td>65%</td>
<td>65%</td>
</tr>
<tr>
<td>CO₂ Capture Rate (%)</td>
<td>N/A</td>
<td>90%</td>
<td>90%</td>
</tr>
<tr>
<td>Gross Plant Power (MWₑ)</td>
<td>491.1</td>
<td>402.3</td>
<td>449.2</td>
</tr>
<tr>
<td>Net Plant Power (MWₑ)</td>
<td>462.1</td>
<td>329.3</td>
<td>381.2</td>
</tr>
<tr>
<td>Capital c/kWh</td>
<td>3.43</td>
<td>5.47</td>
<td>4.49</td>
</tr>
<tr>
<td>Production c/kWh</td>
<td>2.08</td>
<td>3.24</td>
<td>2.98</td>
</tr>
<tr>
<td>Total c/kWh</td>
<td>5.51</td>
<td>8.73</td>
<td>7.46</td>
</tr>
<tr>
<td>Increase in COE (%)</td>
<td>N/A</td>
<td>58.4%</td>
<td>35.4%</td>
</tr>
<tr>
<td>$/ton CO₂ Removed</td>
<td>N/A</td>
<td>29.19</td>
<td>17.72</td>
</tr>
</tbody>
</table>

The cost and power performance values shown in this report were calculated using data and assumptions based on the desire to evaluate an nth plant design for the Dry Carbonate Process. Some assumptions were made as improvements over the data presented in this report, however, it is a reasonable expectation that performance and cost data will improve as the Dry Carbonate Process matures. In addition, contingency factors were applied to cost values in order to accommodate uncertainties in estimates. It is anticipated that further development of the Dry Carbonate Process will further increase its economic advantage over MEA systems. The main areas of improvement for the Dry Carbonate Process are anticipated to be the following:

- More significant heat integration
- Higher sorbent-loading capacity
- Lower pressure drop across the system
- Use of lower value (lower pressure) steam for regeneration
2.0 Introduction

Global warming—increasingly thought to be associated with the atmospheric emission of greenhouse gases (GHGs), principally CO₂—is emerging as the key environmental issue of the early 21st century. The average atmospheric concentration of CO₂ has increased from 280 parts per million (ppm) to 370 ppm since the beginning of the industrial revolution. During that same period, the average global temperature has increased by as much as 1°C (Berger, 2002). Continued uncontrolled emission of GHGs may lead to increased sea levels and increased frequency and intensity of climatic extremes, such as hurricanes and floods.

Fossil fuels used for power generation and transportation, and by industry are the primary sources of anthropogenic CO₂ emissions to the atmosphere. Although there are many potential approaches to limiting GHG emissions, including increased energy efficiency and use of carbon-free or low-carbon fuels, it is becoming increasingly clear that CO₂ capture and sequestration must play an important role in solving the global warming problem. Initial CO₂ capture efforts will no doubt focus on large, stationary sources, with fossil fuel–fired power plants being obvious prime targets. New technologies, including oxygen (O₂) combustion with CO₂ recycle (Douglas et al., 2003), precombustion decarbonization (Doctor et al., 2001), and chemical looping combustion (Hurst et al., 2003; Yu et al., 2003) are under development. These technologies, in addition to being expensive and energy intensive, cannot generally be retrofitted to the large number of existing power plants.

The only currently available process for capturing CO₂ from flue gas that can also be retrofitted to existing plants is based on amine scrubbing. For example, the Econamine FG Plus process (Reddy et al., 2003), which uses a solvent of MEA with an oxidation inhibitor, has been used commercially for CO₂ recovery from specialty chemical plants (not full-scale power plants). Amine-based scrubbing processes, however, are costly and energy intensive because of the large volume of gas to be treated, the low partial pressure of CO₂ in the flue gas, the presence of contaminants that may be detrimental to the solvent, and the energy demand associated with solvent regeneration.

The RTI Dry Carbonate Process for CO₂ capture is based on the use of dry, regenerable sorbents, such as Na₂CO₃, to remove CO₂ from flue gases. Sorbent regeneration produces a gas stream containing only CO₂ and water (H₂O). Condensation of H₂O produces a pure CO₂ stream suitable for subsequent use or sequestration. This process is an “end-of-pipe” technology that can be retrofit into a fossil fuel burning power plant as shown in Figure 1. Specifically, the Dry Carbonate Process can be operated as shown in Figure 2.
Figure 1. Power plant incorporating RTI’s Dry Carbonate Process.

Figure 2. Schematic of RTI’s Dry Carbonate Process.
The Dry Carbonate Process is particularly suited for coal-fired power plants incorporating wet flue gas desulfurization and natural gas–fired power plants, and can be retrofitted to existing plants. The important reactions involved in the capture of CO₂ using Na₂CO₃-based sorbents result in the reversible formation of NaHCO₃ and/or Wegscheider’s salt (Na₂CO₃•3NaHCO₃):

\[
\begin{align*}
\text{Na}_2\text{CO}_3(s) + \text{CO}_2(g) + \text{H}_2\text{O}(g) & \leftrightarrow 2\text{NaHCO}_3(s) \quad \Delta H_r^o = -32.4 \text{ kcal/mol CO}_2 \\
\text{Na}_2\text{CO}_3(s) + 0.6 \text{ CO}_2(g) + 0.6 \text{ H}_2\text{O}(g) & \leftrightarrow 0.4[\text{Na}_2\text{CO}_3•3\text{NaHCO}_3(s)] \quad \Delta H_r^o = -32.5 \text{ kcal/mol CO}_2
\end{align*}
\]

Several patents (Krieg et al., 1984; Sarapata et al., 1987; and Falotico, 1993) describe processes and process improvements to optimize Reaction 1. Both forward reactions are exothermic; therefore, heat management will be an important consideration in a commercial system. Other potential reaction products, such as sodium sesquicarbonate (Na₂CO₃•NaHCO₃•2H₂O) and sodium bicarbonate hydrate (NaHCO₃•2H₂O) were found to be of negligible importance at the reaction conditions of interest. Thermodynamically, Wegscheider’s salt is favored at reaction temperatures of 70°C and above at the H₂O and CO₂ partial pressures studied.

Potential contaminants present in flue gas, such as SO₂ and HCl, react irreversibly with Na₂CO₃ at process conditions according to the following reactions:

\[
\begin{align*}
\text{Na}_2\text{CO}_3(s) + 2\text{HCl}(g) & \rightarrow 2\text{NaCl}(s) + \text{CO}_2(g) + \text{H}_2\text{O}(g) \\
\text{Na}_2\text{CO}_3(s) + \text{SO}_2(g) + \frac{1}{2} \text{O}_2(g) & \rightarrow \text{Na}_2\text{SO}_4(s) + \text{CO}_2(g)
\end{align*}
\]

Formation of NaCl and Na₂SO₄ reduces the capacity of the sorbent for subsequent CO₂ capture. However, the relative concentrations of HCl and SO₂ are an order of magnitude lower than the CO₂ present in flue gas following wet FGD treatment.

This report describes thermogravimetric analyses (TGAs); fixed-bed and fluidized-bed microreactor testing; bench-scale co-current downflow reactor testing; pilot-scale, entrained-bed testing; and bench-scale demonstration testing using actual natural gas–derived and coal-derived flue gases. Per DOE/NETL reporting requirements, this report covers in detail the period of performance from October 1, 2004, through June 30, 2007, by RTI International (RTI). A summary of the research conducted before October 1, 2004 (i.e., September 1, 2000, to September 30, 2004) is provided in Section 2.1. Detailed results and discussion of the prior performance period can be found in previous quarterly and topical reports. Also included in this report is an economic analysis of a commercial-scale version of the Dry Carbonate Process.
2.1 Summary of Research Conducted Between September 1, 2000, and September 30, 2004

Initial research on the Dry Carbonate Process was conducted using TGA to gain a full understanding of the reaction chemistry involved as well as to prove the feasibility of a sodium carbonate–based material to remove CO2 under realistic flue gas conditions (Green et al., 2004). Sorbent precursors used in the preliminary research included various grades of sodium bicarbonate and trona. Trona (Na2CO3•NaHCO3•2H2O) is a naturally occurring mineral that, when heated, decomposes to form sodium carbonate. Subsequent CO2 adsorption can be performed according to Reactions 1 and 2.

Based on observations from TGA studies, RTI and Louisiana State University (LSU) designed and performed several fixed-bed and fluidized-bed tests under simulated flue gas conditions for the adsorption and regeneration reactions. The goal of this effort was to measure the extent of CO2 removal capacity of the carbonate sorbents as well as evaluate their performance over several cycles. Highlights of these studies include the following:

- CO2 removal of greater than 90\% was achieved and is anticipated to be feasible in a commercial system.
- No deactivation of the sorbent was observed over 15 cycles.
- Rapid initial CO2 removal rates were observed in fluidized-bed testing.
- Significant temperature rise was observed during adsorption, causing a decline in CO2 removal rates.

Results of the fixed-bed and fluid-bed studies were encouraging in that they demonstrated that 80 – 90\% of CO2 in simulated flue gas can be removed using the carbonate sorbent – as exhibited in Figure 3. Also, no loss in adsorption performance in 15 subsequent cycles suggests that the sorbent can be reused without needing frequent replacement or “make-up” (Green et al., 2004). However, it was observed from the collected data that fixed-bed and dense-
phase fluid-bed systems are not the optimal reactor schemes for the Dry Carbonate Process. CO₂ removal of 90% cannot be maintained over a long-term run, because the poor heat transfer and poor heat removal inherent in these systems cause the reaction rates to slow and eventually cease. To be commercially feasible, the Dry Carbonate Process must be based on a system that can distribute and remove heat very effectively, as well as perform adsorption and regeneration in a continuous fashion. Several designs that were considered are described in this report.

Fluidized-bed studies conducted by RTI have shown that calcined sodium bicarbonate and calcined trona exhibit high initial CO₂ reaction rates. However, these materials are inherently physically weak and are likely to break down within the types of reactor systems being considered for the Dry Carbonate Process (i.e., processes with constant circulation and fluidization). Therefore, the reactive carbonate material must be placed on a support material in order to achieve the required attrition resistance.

RTI has developed a supported carbonate sorbent that is optimized for attrition resistance and is capable of greater than 90% CO₂ removal from simulated and actual flue gas streams. Over 70 experimental sorbents were developed as part of this research effort. RTI compared the benefits and drawbacks of different support materials, preparation methods, ratios of carbonate and support, and carbonate precursors, and of pH adjustment during preparation. Screening tests were used to eliminate any sorbents that did not meet the desired reactivity, attrition resistance, surface area, and/or particle size distribution. The most promising sorbents were then subjected to fluidized-bed testing in simulated flue gas to provide a more realistic measure of sorbent performance. These efforts led RTI to develop a sorbent that is suitable for use in a commercial entrained-bed-type reactor. To prove this (and to gain valuable knowledge regarding sorbent life and real-life reactivity), RTI subjected the sorbent to testing in a pilot-scale entrained-bed reactor at the CANMET Energy Technology Centre (CANMET) in Ottawa, Ontario, Canada.

3.0 Experimental

3.1 Entrained-Bed Testing

Pilot-scale, entrained-bed testing of RTI’s most promising supported sorbent was conducted at CANMET in Ottawa, Ontario. CANMET, part of Natural Resources Canada, modified their “mini” circulating fluidized-bed combustor to accommodate the testing of RTI’s sorbent in both adsorption and regeneration mode. A schematic of the modified CANMET system is shown in Figure 3.
CANMET’s “single loop” entrained-bed system consists of a 1 m high, 10 cm inner diameter, electrically heated “fluid bed” section; a 4 m high, 10 cm ID, stainless steel, heat-traced and insulated “riser” section; a 80 cm high cyclone; and a 3.2 m high, 5.1 cm ID, “return leg” section. Simulated flue gas enters the fluid-bed section and passes through a distributor plate that evenly distributes the gas to the sorbent. Sorbent particles are added to the system through a feed port and enter the entrained-bed system at the bottom of the riser. With the proper gas flow rate, the particles become entrained in the flue gas and flow up through the riser section. Instrumentation ports for thermocouples and pressure transmitters are distributed at approximately 30 cm intervals over the height of the riser section. The flue gas (along with the sorbent particles) exits tangentially at the top of the riser into the cyclone.

![CANMET’s pilot-scale, entrained-bed reactor.](image)

The cyclone is designed to remove 100% of particles larger than 40 µm from the flue gas. All particles larger than 40 µm (and most above 20 µm) are directed to the return leg section. Only the very fine particles exit with the flue gas and pass through a bag house for fine particle removal. The purpose of the return leg is to transport the captured particles from the cyclone and reinject them into the riser section. The unit consists of a 2.1 m drop pipe from the bottom of the cyclone to the injection system. The drop pipe contains a diverter valve that allows material to be sampled when required. At the base of the drop pipe, the captured solids are blown through a 90-degree elbow (L-valve) by nitrogen injection into the riser.
All data acquisition signals are sent to an HP3497A data acquisition module for processing. The HP3497A transmits all data to and from a personal computer running LabView. CO₂ concentrations in the outlet flue gas are monitored using a non-dispersive, infrared CO₂ analyzer. The main gas-sampling port is located in the cyclone outlet piping.

The entrained-bed testing procedure involved cycling the sorbent between adsorption and regeneration. For an adsorption test, the system is first stabilized at adsorption conditions without the sorbent present. Adsorption is conducted at 55°C (± 5°C) with 3 to 10 vol% CO₂ in a flue gas stream saturated with water vapor (balance nitrogen). The circulation flow rate is usually 200–270 L/min. Once the system is stable at these conditions, roughly 4 to 6 kg of sorbent is introduced to the riser through the solids feed port. Changes in CO₂ concentration, pressure, and temperature are monitored using LabView. The adsorption test was ended when the CO₂ concentration in the outlet flue gas was stable at the inlet flue gas concentration. The sorbent was then unloaded from the system and weighed. At this point, a sample was taken for particle size analysis using a Sympatec-Helos laser diffraction particle analyzer.

Regeneration was conducted in a fluidized-bed mode rather than full circulation to save time and increase the number of adsorption/regeneration cycles. During a regeneration test, the entire system remained at about 55°C (adsorption temperature), except for the fluidized-bed section (where all of the sorbent is contained when slumped), which was heated to 160° to 180°C. These “pre-set” temperatures were higher than typical regeneration temperatures, because a large amount of ambient temperature sorbent was added to the fluidized-bed section, causing the temperature to decrease significantly. The goal was to maintain a regeneration temperature above the adsorption temperatures of 60° to 80°C for the entire test. Nitrogen was passed through the fluidized-bed section at a flow rate of 100 to 130 L/min. Once the system was stable at these conditions, the carbonated sorbent was introduced into the fluidized-bed section through the solids feed port. The sorbent remained fluidized for the length of the regeneration cycle. CO₂ concentration in the outlet gas stream was monitored. The run was ended when the CO₂ concentration returned to 0%. The sorbent was again unloaded from the system and weighed, and a sample was taken for particle size and attrition analyses.

Results of CANMET entrained-bed testing are detailed in Section 4. See Green et al., 2005b; Green et al., 2005d; and Nelson et al., 2005 for additional results and discussion.

3.2 Downflow Reactor Testing at RTI International

Following CANMET testing, there were still engineering challenges that needed to be addressed in order to design a commercially viable Dry Carbonate Process. The challenges included designing a
system to effectively use low value, low grade heat for sorbent regeneration, minimizing the additional power required by the plant’s induced draft fan due to inclusion of the Dry Carbonate Process, and effectively moving the sorbent between adsorption and regeneration. To this end, RTI conceptualized a new process design. This new process utilizes a co-current downflow gas-solid contacting scheme rather than an up-flow scheme of a more traditional “transport” reactor. This design will minimize the power loss associated with the induced draft fan. Economic analyses of a commercial-scale Dry Carbonate Process (as detailed in Section 5) shows that this design incurs roughly a 1.4 psia pressure drop across the system - requiring 13,664 kW_e auxiliary power load for the induced draft fans. This represents roughly a 31% power savings over a commercial MEA system which incurs a 19,880 kW_e power load by the induced draft fans. This process design also incorporates screw conveyor systems to both lift and regenerate the sorbent. Low pressure steam can be condensed on the inside of the screw conveyor jacket and shaft to effectively transfer heat to the sorbent particles. The reactivity and attrition data collected from the CANMET entrained-bed testing was used to accurately design and size a bench-scale unit for testing at RTI. Before this “integrated” unit was constructed, RTI first tested the various components of the new process design to confirm that each component worked separately as expected.

RTI designed and constructed a 3-inch diameter atmospheric pressure co-current downflow reactor system and conducted a series of tests to determine the rate of reaction of the Na_2CO_3-based supported sorbent with CO_2 and water vapor. The reactor system is shown in Figures 4 and 5. The center section of the reactor is enclosed by a single-zone, 3 ft clamshell furnace. The gas-feed system for this reactor system begins with a pair of MFCs for metering in CO_2 and nitrogen. The gas from the MFCs flows into the lower inlet of the liquid vaporizer system, which is heated externally by heat tapes and internally by a small heating rod. Liquid water is fed into the vaporizer with a positive displacement pump. As the liquid vaporizes, the vapor is swept up and out of the vaporizer with the gas flow. The preheated feed gas/vapor mixture enters the upper section of the reactor below the sorbent entrance point. Sorbent is fed from a hopper at the top of the reactor through a valve by gravity. To improve the reliability of the sorbent flow, the ball valve that was initially used was replaced with a gate valve (following Test #8). At that point, the use of aeration nitrogen shown in Figure 5 was discontinued. Sorbent flow is started after the flows of CO_2 and N_2 are established. The sorbent collects in a bucket at the bottom of the reactor. The sorbent flow rate is calculated by weighing the collected sorbent at the end of each test. The equipment was also modified after Test #8 to include a digital scale under the sorbent collection bucket to provide a better indication of sorbent flow as a function of time. The temperature of the collected sorbent was monitored with a thermocouple. The gas exiting the reactor passes through a condenser to a non-dispersive infrared CO_2 analyzer. The sorbent is regenerated between tests and reused.
Figure 4. Bench-scale co-current downflow reactor system as constructed at RTI.
Figure 5. Schematic of the co-current downflow reactor system.
Initially, the reactor was operated with sand to establish the conditions necessary for good solids flow and to test the gas delivery and gas analysis systems. One test was conducted with calcined trona (Grade T-50), which absorbed little or no CO₂ in the short reactor residence time. Fifteen tests were then conducted with SCI-012705-1 sorbent, composed of 15% Na₂CO₃ on an inert support. One additional test was conducted with a new batch (SCI-090905-1) of supported sorbent.

Three tests were conducted using calcined sodium bicarbonate (a mixture of Grade 3 and Grade 5) as the sorbent. The sorbent was regenerated between tests and reused in subsequent tests conducted with the reactor system at a temperature of 25°C. Preheated water was added to the simulated flue gas to supersaturate it. Water in excess of the saturation concentration (approximately 3.1 vol%) was assumed to be absorbed by the sorbent. Therefore, the flue gas composition was assumed to be 11% CO₂, 3.1% water vapor, and a balance of nitrogen.

3.3 Field Test of Heated Screw Conveyor Regeneration

A field test program was conducted to determine whether a Na₂CO₃-based supported sorbent could be satisfactorily regenerated during passage through a heated screw conveyor. Regeneration testing was conducted at the facilities of Therma-flite, Inc., in Benicia, California. A supported sorbent (SCI-090905-1), composed of 10% Na₂CO₃ on a ceramic support, was used. Sorbent properties are provided in Table 1. Properties of a previous batch of sorbent (SCI-012705-1) that was used in the entrained-bed testing at CANMET Energy Technology Centre are included for comparison. SCI-012705-1 contains 15% Na₂CO₃ by weight, thus it would be expected that SCI-090905-1 would have greater porosity and higher surface area, given the lower Na₂CO₃ content.

<table>
<thead>
<tr>
<th>Table 1. Comparison of Supported Sorbent Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Sorbent</strong></td>
</tr>
<tr>
<td>Na₂CO₃ Content, %</td>
</tr>
<tr>
<td>Surface Area, m²/g</td>
</tr>
<tr>
<td>Bulk Density, g/cc</td>
</tr>
<tr>
<td><strong>Porosimetry</strong></td>
</tr>
<tr>
<td>Total Intrusion Volume, cc/g</td>
</tr>
<tr>
<td>Total Pore Area, m²/g</td>
</tr>
<tr>
<td>Median Pore Diameter (V), Å</td>
</tr>
<tr>
<td>Median Pore Diameter (A), Å</td>
</tr>
<tr>
<td>Average Pore Diameter (4V/A), Å</td>
</tr>
<tr>
<td>Bulk Density, g/cc</td>
</tr>
<tr>
<td>Apparent Density, g/cc</td>
</tr>
<tr>
<td>Porosity, %</td>
</tr>
</tbody>
</table>
Before the Therma-flite field test, the SCI-090905-1 sorbent was run through a series of carbonations in RTI’s downflow contactor. The sorbent was essentially completely loaded with CO₂ before regeneration testing.

The tests were conducted in Therma-flite’s dual-screw, bench-scale testing screw conveyor, which is approximately 5 feet long and contains two “holo-flite” screws that rotate together and are housed in a metal jacket. The conveying speed is set by adjusting a variable speed motor which drives both screws. The system’s jacket has three vent ports at approximately 1.5 feet, 3 feet, and 4.5 feet from the feed end of the conveyor. Sorbent temperature can be measured through these three ports using a handheld thermocouple. The bench-scale unit also has a feed inlet port and an outlet port. The system is heated by tempered oil that flows through the inside of the screw shafts and flights. The jacket is solid metal and is therefore not heated with oil. Figures 6 and 7 show Therma-flite’s testing system. Testing was done in a horizontal configuration, because no vertical testing conveyors were available.
3.3.1 Regeneration Tests

A total of seven regeneration tests were conducted. The desired regeneration temperature was 120°C. Since the vent ports provided an escape route for some heat, a higher oil temperature was used to compensate for heat loss. System settings for each regeneration test are listed in Table 2.

As an example of a typical regeneration test, Test #1 was performed as follows: approximately 31.5 pounds of room temperature sorbent were introduced to the heated screw conveyor. Since the screws are configured horizontally and the system jacket is not flush against the screws, a portion of the initial feed lined the bottom of the test unit and essentially remained there through all subsequent tests. Roughly 14 pounds of sorbent were collected at the system outlet port during Test #1. In addition, three samples, labeled #1, #2, and #3, were collected during Test #1 for further analysis at RTI: (1) when the sorbent first began to flow through the outlet port, (2) at approximately the middle of the test, and (3) when the outlet flow was nearly finished. The “sorbent residence time” refers to the difference between the time at which the sorbent was added and the time at which the sorbent first started flowing through the outlet port. (Note that the Test #1 residence time is much longer than for other tests with the same motor speed. This is because Test #1 was the only test in which sorbent first lined the bottom of the apparatus before it was conveyed to the outlet port.)
Table 2. Regeneration Test Conditions in Therma-flite’s Bench-Scale Screw Conveyor

<table>
<thead>
<tr>
<th>Test</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sorbent Source</td>
<td>Bucket 1 “system prime”</td>
<td>Bucket 2 1st pass</td>
<td>Bucket 3 1st pass</td>
<td>Bucket 3 2nd pass</td>
<td>Buckets 1 &amp; 2 2nd pass</td>
<td>Bucket 3 3rd pass</td>
<td>Buckets 1 &amp; 2 3rd pass</td>
</tr>
<tr>
<td>Sorbent residence time (min:sec)</td>
<td>5:30</td>
<td>3:50</td>
<td>2:45</td>
<td>2:45</td>
<td>3:50</td>
<td>NA</td>
<td>2:45</td>
</tr>
<tr>
<td>Rotation Rate (rpm)</td>
<td>6</td>
<td>6</td>
<td>8</td>
<td>8</td>
<td>6</td>
<td>4</td>
<td>8</td>
</tr>
<tr>
<td>Vertical Pitch (deg)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Mass at inlet (lbs)</td>
<td>31.5</td>
<td>25</td>
<td>29</td>
<td>~24</td>
<td>~38</td>
<td>~24</td>
<td>~38</td>
</tr>
<tr>
<td>Mass at outlet (lbs)</td>
<td>14</td>
<td>24</td>
<td>24</td>
<td>~24</td>
<td>~38</td>
<td>~24</td>
<td>~38</td>
</tr>
<tr>
<td>Oil set point temperature (deg C)</td>
<td>149</td>
<td>149</td>
<td>149</td>
<td>149</td>
<td>149</td>
<td>149</td>
<td>166</td>
</tr>
<tr>
<td>Inlet sorbent temperature (deg C)</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>49</td>
<td>50</td>
<td>50</td>
<td>55</td>
</tr>
<tr>
<td>Screw surface temperature (deg C)</td>
<td>120</td>
<td>120</td>
<td>120</td>
<td>120</td>
<td>120</td>
<td>120</td>
<td>NA</td>
</tr>
<tr>
<td>Samples (sample #)</td>
<td>1,2,3</td>
<td>4,5,6</td>
<td>7,8</td>
<td>9,10</td>
<td>11,12</td>
<td>13,14</td>
<td>15,16</td>
</tr>
<tr>
<td>Sampling Notes</td>
<td>Samples taken at beginning, middle, and end of output</td>
<td>Beginning middle, and end</td>
<td>Beginning and end</td>
<td>Beginning and end</td>
<td>Middle end</td>
<td>Beginning and end</td>
<td>Beginning and end</td>
</tr>
</tbody>
</table>

The samples collected from Tests #1 through #6 were analyzed at RTI to determine the extent of decarbonation and degradation. The amount of CO2 released during Test #1 was calculated by heating a sample from Test #1 in the TGA system and measuring the weight loss. This weight loss was then compared to the weight loss experienced by a fresh (fully carbonated) sample. The TGA procedure involved loading a sample into the TGA system, heating to 120°C in N2 until a constant weight was observed, and then heating to constant weight at 160°C in N2.

A relative measure of attrition was established by determining the particle size distribution (using a Sympatec HELOS laser diffraction system) of each sample and comparing it to the “fresh” sample.

### 3.3.2 Sorbent Cycling Tests

All of the sorbent from the previous tests was combined for multicycle sorbent degradation testing. The combined sorbent was conveyed through the heated screw conveyor system 20 times in succession. The hollow screws were heated to 149°C and were set to a rotational speed of 8 rpm for the multicycle testing. Samples were taken after Cycle number 1, 5, 10, and 20. These samples were sent to RTI for TGA, thermally programmed desorption (TPD)/mass spectroscopy, and particle size analysis. The main objective of these multicycle tests was to see whether significant attrition of the sorbent...
occurred during multiple passes through the screw conveyor system. Relative degradation was characterized by particle size analysis.

### 3.3.3 Sample Identification

A sample identification key is provided in Table 3.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Therma-flite Sample Number</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>100705a-PreTF</td>
<td>NA</td>
<td>Carbonated SCI-090905-1 (Pre Therma-flite)</td>
</tr>
<tr>
<td>101205a-TF</td>
<td>1, 2, 3</td>
<td>Test #1 samples</td>
</tr>
<tr>
<td>101205b-TF</td>
<td>4,5,6</td>
<td>Test #2 samples</td>
</tr>
<tr>
<td>101205c-TF</td>
<td>7,8</td>
<td>Test #3 samples</td>
</tr>
<tr>
<td>101205d-TF</td>
<td>9,10</td>
<td>Test #4 samples</td>
</tr>
<tr>
<td>101205e-TF</td>
<td>11,12</td>
<td>Test #5 samples</td>
</tr>
<tr>
<td>101205f-TF</td>
<td>13,14</td>
<td>Test #6 samples</td>
</tr>
<tr>
<td>101205g-TF</td>
<td>15,16</td>
<td>Test #7 samples</td>
</tr>
<tr>
<td>101205h-TF</td>
<td>17</td>
<td>Multicycle #1 sample</td>
</tr>
<tr>
<td>101205i-TF</td>
<td>18</td>
<td>Multicycle #5 sample</td>
</tr>
<tr>
<td>101205j-TF</td>
<td>19</td>
<td>Multicycle #10 sample</td>
</tr>
<tr>
<td>101205k-TF</td>
<td>20</td>
<td>Multicycle #20 sample</td>
</tr>
</tbody>
</table>

### 3.4 Integrated Downflow Adsorber with Continuous Regeneration

Following separate, successful evaluations of the downflow adsorber and the screw conveyor regenerator, an “integrated unit,” including two vertical screw conveyors and a downflow adsorber, was assembled at RTI. A schematic of this system is shown in Figure 8. Figure 9 shows the integrated unit as constructed at RTI.

This integrated unit includes a 4-inch diameter polycarbonate adsorber and two 8-inch diameter by 6-foot-long carbon steel jacketed screw conveyors for sorbent regeneration and cooling. The regeneration screw conveyor has a hollow shaft in addition to the jacket for added heat transfer area. The screws are driven by two 2-horsepower, 3-phase motors equipped with variable frequency drives (VFDs) to allow for speed adjustment, thus controlling the flow rate of the sorbent material. A Sussman MBA-3 electric boiler provides the heat required for sorbent regeneration. This 3 kW boiler can produce up to 9 lb/hr of saturated steam at pressures as high as 90 psig. A steam trap installed at the outlet of the steam jacket ensures that all steam condenses on the heat transfer surfaces. Steam condensate flows by gravity through an air-cooled heat exchanger into a floor drain. Both the flue gas and the CO₂ rich regeneration gas vent through exhaust ducts. A gas sample is drawn through a series of filters by a Gast oilless
diaphragm pump, model DOA-P704-AA. A Horiba NDIR analyzer determines the CO₂ content of the sample. All instrument signals, including those from the analyzer, are relayed through chained input/output (I/O) modules using Modbus protocol to a personal computer data logger running National Instruments Lookout software.

![Figure 8. Schematic of integrated adsorber/regenerator system.](image-url)
Upon initial shakedown of the integrated system, the sorbent flow rate became inconsistent after CO₂ and water vapor were introduced. In some cases, plugs developed and sorbent circulation stopped. Flow distributors were installed at the inlet and discharge from the lower (“heated”) screw and at the inlet to the upper (“cooled”) screw. The flow distributor consisted of six lengths of 1/8-inch stainless steel tubing in which holes were drilled at 1 inch spacing. The open ends of the tubing were crimped to direct a total of approximately 3.5 standard liters per minute (SLPM) of aeration gas through 30 holes. The flow distributor assemblies were inserted into the screw housings through bulkhead fittings. The flow distributors were oriented so that the aeration gas was directed vertically downward to impinge on the
lower surface of the screw housings. The two screws were operated independently, and sorbent flow rate versus power input curves were developed for each screw with the newly installed flow distributors.

3.4.2 Heat Transfer Capability of the Heated Screw Conveyor

Several tests were conducted to determine the heated screw conveyor’s capacity to transfer heat to the sorbent particles. Of particular interest was the temperature of the sorbent bulk at the outlet of the heated screw conveyor. The heated screw conveyor was operated with 50 psig of saturated steam as the heating medium. RTI’s supported sorbent, SCI-022806-1, flowed downwards through the adsorber concurrently with simulated flue gas.

3.4.3 Initial CO₂ Capture Tests with Modified and Improved Integrated Unit

Additional modifications and improvements made to the integrated system include the following:

1. A Laboport Model N86KTP vacuum pump was installed at the outlet of the heated screw conveyor, replacing the original venturi system. This improved the disengagement of the regeneration off-gas and prevented the off-gas from carrying over into the sorbent cooler.

2. The shaft seal located at the bottom of the heated screw conveyor failed because of wear associated with the accumulation of sorbent. The damaged seal is shown in Figure 10. This resulted in unreliable sorbent flow and sorbent leakage from the integrated system. This seal was replaced with a more robust, engineered seal composed of a segmental bushing, a lantern ring, and a bearing.

With these modifications in place, two 8-hour periods of continuous solids circulation were completed. RTI also conducted several shakedown CO₂ removal tests to confirm the effective operation of system components, such as the sorbent regenerator, sorbent cooler, steam generator, and CO₂ analyzer.

A 96-hour continuous sorbent circulation test of the integrated system was used to establish flow consistency. Sorbent was circulated through the downflow adsorber, the heated screw conveyor regenerator, and the water cooled screw conveyor sorbent cooler. During this test, simulated flue gas was introduced to the downflow adsorber for two periods of approximately 4 hours each. The carbon dioxide concentration of the treated flue gas was measured continuously during these periods. Carbon dioxide removal was confirmed. Continuous sorbent flow, with no clogging or plugging of the screws, was maintained over the entire 96-hour period.
3.4.4 Testing Sorbent Regeneration to Improve CO$_2$ Adsorption in the Integrated System

To test the theory that incomplete regeneration was responsible for decreased CO$_2$ adsorption efficiency, the integrated system was modified to mimic the conditions of the original downflow contactor.

The differences between the downflow contactor used in previous experiments and the integrated unit contactor include the reactor geometry and the means of sorbent regeneration. To determine the effect of these differences, approximately 6 kg of sorbent was removed from the integrated unit and calcined in a convection oven for 5.5 hours at 150°C. A funnel was placed at the top of the integrated unit’s contactor, with a restriction fixed to the funnel outlet to control sorbent flow. Simulated flue gas was introduced into the system, and solids introduced shortly thereafter. The screw conveyors were not operated. Results of this testing are presented in Section 4.4.4.

3.5 Installation of RTI’s Integrated System into EPA’s Multipollutant Control Research Facility

After shakedown and testing in RTI’s laboratory, the integrated system was moved to the U.S. Environmental Protection Agency’s (EPA’s) Multipollutant Control Research Facility (MPCRF), a part
of the EPA’s Air Pollution Prevention and Control Division (APPCD) in Research Triangle Park, NC. ARCADIS, Inc., EPA’s on-site contractor, interfaced with RTI to help install and test the integrated system at the U.S. EPA site.

The MPCRF includes a 4 MMBtu/hr multifuel furnace (gas, oil, and coal), thermodynamic load simulation, an electrostatically enabled fabric filter, and a lime slurry wet scrubber, as shown in Figure 11.

![Figure 11. Basic schematic of the U.S. EPA’s MPCRF equipped with RTI’s carbon dioxide capture system.](image)

The refractory-lined vertical furnace is fed by a multifuel burner mounted at the top. The burner design is based on the “movable block swirl adjustment technology” developed by the International Flame Research Foundation (IFRF). All fuel feed systems are connected to a single flame safety system, and can be selected individually or in any co-firing combination. All air and fuel flows are measured by
the facility’s OPTO-22 control system and recorded by the facility’s supervisory control and data acquisition (SCADA) computer. Manual valves control the firing rate for gas and oil, but a precise loss-of-weight feed system (which receives its set point from the SCADA computer) controls the coal feed. Secondary combustion air is controlled by a VFD that alters the rotational speed of the supply blower in response to the output of a proportional/integral/derivative (PID) controller built into the OPTO-22 system.

The thermodynamic load simulators cool the combustion gases in a way that mimics the equipment at a coal-fired industrial boiler. The first “load” consists of a series of exposed cooling water pipes inside the combustor itself, simulating the “wet wall” of a boiler. The superheater simulator, the first of three air/water heat exchangers is attached directly to the furnace outlet. From there, the combustion gases are ducted to a pair of heat exchangers which simulate an economizer (boiler feed water pre-heater). One of these two parallel heat exchangers is of an air/air configuration, and can provide pre-heated secondary combustion air to the burner (at a temperature determined by the proportion of combustion gases routed through this unit). The third air/water heat exchanger, downstream of the economizer simulator, simulates the load of an industrial recuperator (air pre-heater). Two PID control loops in the OPTO-22 system control the economizer and recuperator outlet temperatures by adjusting the cooling water flows.

The MPCRF operates in two “modes” based on the research plan for the combustor. During testing, when coal or oil is being combusted, the MPCRF operates approximately 8–12 hours per day. During the remaining time, natural gas is burned to maintain system temperatures and gas flow. During specialized tests, the system operates on natural gas only and is “doped” with surrogate components. The unit is equipped with a flue gas cleaning system (FGCS) consisting of a selective catalytic reduction (SCR) system and an electrostatic fabric filter (ESFF) followed by a lime slurry wet scrubber. At its full firing rate, the flue gas flow is 1,000 standard cubic feet per minute (SCFM).

The MPCRF combustor is sized so that multipollutant flue gas cleaning technologies may be tested, modeled, and scaled up for commercial applications. For wet-dry gas adsorption and electrostatic particle removal technologies, this is typically 1,000–2,000 actual cubic feet per minute (ACFM). In addition, the combustor’s gas velocity and temperature profiles are similar to those of commercial systems. The combustor is able to fire pre-ground (pulverized) coal, distillate oil, and/or natural gas at 2 to 4 million Btu/hr, supplying flue gas at 300°F (150°C) to the MPCRF’s flue gas cleaning system.
RTI’s CO₂ capture system was tested using a slipstream of flue gas obtained downstream of the wet limestone scrubber and upstream of the induced draft (ID) fan. ARCADIS personnel installed the piping and electrical connections that integrated the two systems. The following connections and modifications were made to allow RTI’s test unit to function at the MPCRF:

- unit was connected to 100 A, 3-phase, 208 V electrical service
- the flue gas line leading to compressor was insulated
- vent lines for “treated” flue gas and regeneration off-gas were installed
- piping for cooling water and steam boiler feed was installed
- drain lines for cooling water and steam condensate were connected
- piping for compressed air line was installed

A ¾ HP Gast rotary vane compressor pulled the scrubber exhaust sample from the MPCRF exhaust duct through a heated line into the co-current downflow adsorber. The flue gas from the MPCRF was saturated with water at a temperature of 55° to 67°C. The flow rate of the flue gas was measured with a rotameter. Very little water condensation was observed in the rotameter or in the adsorber.

3.6 Effects of Flue Gas Contaminants on a Sodium Carbonate Sorbent

3.6.1 Reactions of Sulfur Dioxide with Sodium Carbonate Sorbent

3.6.1.1 LSU Electrobalance (TGA) Studies

The effect of SO₂ in the flue gas was investigated using TGA. Expected reactions with the sorbent were

\[
\text{Na}_2\text{CO}_3 + \text{SO}_2 \rightarrow \text{Na}_2\text{SO}_3 + \text{CO}_2 \tag{5}
\]

and

\[
\text{Na}_2\text{CO}_3 + \text{SO}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{Na}_2\text{SO}_4 + \text{CO}_2 \tag{6}
\]

The effect of SO₂ addition, with and without free O₂ present, was examined. When 0.4% and 0.2% SO₂ were added, the tests were terminated after three cycles. The remaining tests, in which 0.1% SO₂ was added, continued through five cycles. The adsorption cycles were conducted at 70°C, and the sorbent was regenerated at 120°C in helium. Only the carbonation gas composition varied. Calcined Grade 3 sodium bicarbonate (SBC#3) was used in six tests, and calcined trona was used in one test. The use of unsupported sorbents for this testing allowed a greater period of exposure (5 times as many cycles) before the sorbent was completely deactivated. Details and discussion of these results are provided in
Section 4.6. From these results it is clear that when sulfur-containing fossil fuels are burned, the CO₂ capture step must be downstream of a desulfurization step.

3.6.1.2 RTI Fluid-Bed Reactor Studies

A series of bench-scale fluidized-bed tests was conducted in a 1-inch diameter quartz reactor. The reactor system used is similar to that shown in Figure 12 below, except that the gas supply system and gas analysis system were changed.
The carbonation gas was supplied from a premixed cylinder containing 12% CO₂, 250 ppmv SO₂, and balance N₂. The gases exiting the reactor were routed to a gas chromatograph for determination of SO₂ and CO₂ at intervals of 2 to 3 minutes.
Grade 5 sodium bicarbonate (SBC#5) was calcined in the reactor before testing began and then subjected to five adsorption/desorption cycles. Two carbonation cycles were conducted without steam addition, and in the remaining carbonation cycles, 10% H₂O was added. Carbonation was conducted at 60° to 70°C at a flow rate of 2 SLPM (dry basis), equivalent to a superficial velocity of 1.0 ft/sec. Carbonation tests were terminated after approximately 60 minutes. Desorption was conducted at 140°C in 100% N₂ at 2 SLPM for approximately 60 minutes, and the bed was cooled to 60° to 70°C.

3.6.2 Reactions of Hydrogen Chloride with Sodium Carbonate Sorbent

The effect of HCl in the flue gas was investigated in a bench-scale fluidized-bed reactor system. The expected reaction with the sorbent was

\[
Na_2CO_3 (s) + 2HCl(g) \rightarrow 2NaCl (s) + CO_2 (g) + H_2O (g) \quad (7)
\]

The quartz reactor system shown in Figure 12 was used for these tests. SBC#5 was calcined in the reactor before testing began. A mixture of 100 ppm HCl, 11.7% CO₂, and balance nitrogen was passed through a 3-inch bed of calcined SBC#5 at a superficial velocity of 13 ft/min, resulting in a contact time of approximately 0.9 seconds. HCl in the reactor exit gas was measured by passing the entire gas stream through an impinger containing deionized water and using ion chromatography to analyze sequential impinger samples representing 10 minutes of gas flow.

3.6.3 Mercury Sorption Testing with a Sodium Carbonate Sorbent

Testing was performed to determine whether supported Na₂CO₃-based sorbents are likely to adsorb Hg. Samples of ~0.5 g of material were exposed for 30 minutes to a nitrogen stream containing 460 µg of elemental Hg vapor per dry standard cubic meter at temperatures of 60°C and 300°C. At the completion of the exposure period, the samples were analyzed for Hg content using a Milestone DAM-80 direct Hg analyzer. To verify a material balance, the quality assurance measures included blank runs and analyses of “backup” cartridges of a known Hg sorbent.

Three different formulations were tested: 20% Na₂CO₃ on alumina, 40% Na₂CO₃ on alumina, and 20% Na₂CO₃ on a silica-containing support. A small-scale screening apparatus, shown in Figure 13, was used for this study.
Figure 13. Small-scale mercury adsorption screening apparatus.

The dotted line in Figure 13 indicates equipment that was installed inside a fume hood. An electronic MFC established the flow rate of N₂ across the Hg vapor permeation tube housed in a temperature-controlled Dynacalibrator oven (TIC). Thermocouples (T) monitored the heat tracing of the process lines, and variable transformers (EC) controlled heat-tracing temperature.

4.0 Results and Discussion

4.1 Entrained-Bed Testing

The objective of the entrained-bed testing was to evaluate the performance of RTI’s optimized sorbent in a system that represented the conditions (e.g., flow rate, gas-to-solid contact, circulation) anticipated in a continuous transport-type reactor system. The important performance measures are reactivity and attrition resistance over multiple cycles. Details of the experimental procedures used for entrained-bed testing are provided in Section 3.1.

4.1.1 Single-Cycle Test

In a single-cycle adsorption test, 5.4 kg of supported sorbent was exposed to a simulated flue gas of 3 vol% CO₂ saturated with water vapor (balance nitrogen) at a flow rate of 200 L/min and nominal temperature of 60°C. The CO₂ removal profile and average riser temperature profile for this run are shown in Figure 14. Figure 14 shows one of the benefits of conducting the exothermic carbonation
reaction in an entrained-bed reactor: the system temperature does not rise enough to extinguish the reaction (as was previously seen in fixed-bed and fluidized-bed testing). The temperature rise over the entire 15-minute test was limited to about 4°C in the riser section. Constant sorbent mixing and a dispersed phase (rather than dense sorbent packing) helped dissipate the heat generated during the exothermic reaction. It is also theorized that the support material helped control the temperature rise by providing a sink for the heat generated during CO₂ adsorption.

![Graph](image-url)

**Figure 14. Carbon dioxide concentration of reactor outlet gas during first adsorption cycle of CANMET testing.**

**Figure 15** shows the percentage of CO₂ removed from the simulated flue gas at any given time during adsorption. Ninety percent removal (and above) is achieved for more than 1 minute during this run. These data suggest that the RTI-supported sorbent is capable of 90% CO₂ removal over the entire residence time (5 to 20 seconds) associated with entrained-bed type systems.

The total amount of CO₂ absorbed (based on integration of the CO₂ removal plot in Figure 15) was calculated to be 16.72 L, or roughly 0.75 mols. A quantitative measure of capacity, based on cumulative CO₂ removal, is shown in **Figure 16**.

After the adsorption cycle, the sorbent was removed from the system to prepare the fluidized-bed section for a regeneration test. The fluid-bed section was heated to approximately 180°C, and the “room temperature” sorbent was then fed back into the system. Regeneration was performed in pure nitrogen at a flow of 130 L/min. The release of CO₂ and change in fluid-bed temperature were monitored and are indicated in **Figure 17**.
Figure 15. Carbon dioxide removal in first adsorption cycle.

Flue gas: 3% CO₂, sat. with water vapor, N₂ balance
Flowrate: 200 L/min
Temperature: 60°C (± 2°C)

Flue gas: 3% CO₂, sat. with water vapor, N₂ balance
Flowrate: 200 L/min
Temperature: 60°C (± 2°C)

Figure 16. Cumulative sodium carbonate conversion in first adsorption cycle.
These data show that the average temperature of the fluid-bed decreased significantly when the sorbent was added, but the temperature never dropped within a range where adsorption of CO₂ can be expected (<80°C). For most of the regeneration test, the temperature remained between 140° and 170°C. Integration of the regeneration peak yields a total of 16.88 L CO₂, or roughly 0.75 mols. This amount represents slightly more CO₂ than was shown to be absorbed, but is within expected experimental error, demonstrating a good material balance closure. Not only will the sorbent release CO₂ at these temperatures, it can also be completely regenerated in a short period of time (~10 minutes).

4.1.2 Multicycle Tests

RTI’s supported sorbent was used in a seven-cycle test to assess its multicycle performance. A summary of the test results appears in Tables 4 and 5.

Table 4. Summary of Adsorption Results from Seven-Cycle, Entrained-Bed Test at CANMET

<table>
<thead>
<tr>
<th>Cycle</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ removed (L)</td>
<td>16.72</td>
<td>18.30</td>
<td>17.67</td>
<td>14.11</td>
<td>13.24</td>
<td>15.89</td>
<td>14.97</td>
</tr>
<tr>
<td>% CO₂ removal (maximum)</td>
<td>95</td>
<td>93</td>
<td>94</td>
<td>93</td>
<td>92</td>
<td>92</td>
<td>92</td>
</tr>
<tr>
<td>Length of 90% removal (mins)</td>
<td>1.07</td>
<td>0.64</td>
<td>1.00</td>
<td>0.53</td>
<td>0.43</td>
<td>0.63</td>
<td>0.47</td>
</tr>
<tr>
<td>Initial temperature (°C)</td>
<td>61</td>
<td>60</td>
<td>56</td>
<td>60</td>
<td>64</td>
<td>61</td>
<td>65</td>
</tr>
<tr>
<td>Temperature rise (°C)</td>
<td>4</td>
<td>13</td>
<td>11</td>
<td>10</td>
<td>12</td>
<td>13</td>
<td>11</td>
</tr>
<tr>
<td>Reaction rate (moles/min)</td>
<td>0.258</td>
<td>0.343</td>
<td>0.279</td>
<td>0.248</td>
<td>0.259</td>
<td>0.296</td>
<td>0.272</td>
</tr>
</tbody>
</table>
The data presented in Table 4 show the overall CO\textsubscript{2}-removal performance of the sorbent during each of the seven adsorption runs. In terms of maximum removal achieved and initial reactivity, the sorbent performed quite consistently over all seven cycles. RTI’s sorbent exhibited greater than 90% removal of CO\textsubscript{2} in every cycle and showed negligible drop-off in reactivity over the seven cycles (Figure 18).

In addition to reactivity, a sorbent’s physical strength (attrition resistance) is an important property to optimize for an entrained-bed type system. Davison Index (DI) measurements of the sorbent (before CANMET testing) were very good and indicated that the sorbent might be sufficiently durable for entrained bed operation. In actual testing, relative measures of the physical strength of the supported sorbent remained unchanged over the seven-cycle test. During the CANMET testing, it was not feasible to collect any meaningful data on weight of fines collected in the system’s baghouse. To compensate for this lack of data, two relative measures of attrition were used: (1) sorbent weight loss per cycle and (2) particle size distribution of the sorbent after each cycle.
As noted earlier, 5.4 kg of the RTI sorbent was loaded into the entrained-bed system to start the multicycle tests. After the seventh adsorption cycle, 5.95 kg of sorbent was removed from the system. Some of this excess was due to absorbed CO₂, and it is also possible that some material was left in the system following the initial pretreatment of the sorbent. However, if the sorbent experienced significant attrition during these tests, it was expected that the final sorbent weight would be less than the starting weight of 5.4 kg. These results suggest that the sorbent did not experience significant attrition and can withstand the mechanical stress of an entrained-bed system.

Particle-size analysis of collected samples (up to cycle #5) also suggests that the material is not producing any fines due to attrition. Table 6 presents a comparison of particle-size data collected after the first five cycles.

Table 6. Comparison of Sorbents’ Particle Size after Adsorption/Regeneration Cycles

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Fresh</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>% (mass) of particles &lt;30 µm</td>
<td>2.7%</td>
<td>0.8%</td>
<td>0.9%</td>
<td>1.0%</td>
<td>1.2%</td>
<td>1.5%</td>
</tr>
<tr>
<td>% (mass) of particles &lt;50 µm</td>
<td>19.5%</td>
<td>16.1%</td>
<td>14.1%</td>
<td>20.6%</td>
<td>20.6%</td>
<td>21.4%</td>
</tr>
<tr>
<td>Average particle size (µm)</td>
<td>76.38</td>
<td>78.16</td>
<td>83.87</td>
<td>72.02</td>
<td>72.64</td>
<td>72.30</td>
</tr>
</tbody>
</table>

These data suggest that the sorbent particles are not being converted into finer particles while circulating. The data are consistent over each cycle, and after the first cycle, the average particle size actually increased, possibly suggesting that the fines in the fresh sorbent batch were blown to the baghouse and that no new fines were produced —or that the sorbent particles agglomerated slightly over the five cycles. The percentage of particles smaller than 30 µm showed a negligible increase over five cycles.

4.1.3 Adsorption at Different Carbon Dioxide Concentrations

Additional entrained-bed reactor testing was conducted to evaluate sorbent performance as a function of starting CO₂ concentration in the flue gas. Table 7 summarizes the results of these tests.

Table 7. Comparison of Carbon Dioxide Removal Performance at Different Initial Carbon Dioxide Concentrations During CANMET Testing

<table>
<thead>
<tr>
<th>Starting CO₂ Concentration in Flue Gas</th>
<th>3%</th>
<th>10%</th>
<th>15%</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ removed (L)</td>
<td>16.72</td>
<td>23.32</td>
<td>24.09</td>
</tr>
<tr>
<td>% CO₂ removal (max)</td>
<td>95</td>
<td>71</td>
<td>61</td>
</tr>
<tr>
<td>Time of adsorption (min)</td>
<td>6</td>
<td>3.5</td>
<td>3</td>
</tr>
<tr>
<td>Initial temperature (°C)</td>
<td>61</td>
<td>50</td>
<td>57</td>
</tr>
<tr>
<td>Temperature rise (°C)</td>
<td>4</td>
<td>7</td>
<td>14</td>
</tr>
<tr>
<td>Reaction rate (mols/min)</td>
<td>0.258</td>
<td>0.752</td>
<td>0.978</td>
</tr>
</tbody>
</table>
Higher initial concentrations of CO₂ in the flue gas significantly affect the fraction of CO₂ removed. The fractional CO₂ removal was lower at higher initial concentrations, but both the total mass of CO₂ absorbed and the rate of CO₂ adsorption increased. At an initial CO₂ concentration of 15%, the sorbent removed 61% of the CO₂ passing through the entrained-bed reactor (under the set test conditions).

The improved reactivity at higher CO₂ concentrations is consistent with the previous results obtained during fixed-bed testing (Green et al., 2004), but the extent of the increase in reactivity was not expected. The reactivity at 15% initial CO₂ concentration was nearly four times the reactivity exhibited at 3% initial CO₂ concentration. A graphical comparison of the reactivity results appears in Figure 19.

4.1.4 Comparison of RTI’s Supported Sorbent to Unsupported Sorbents

A single adsorption/regeneration cycle at 3% initial CO₂ concentration was conducted for both calcined trona and calcined sodium bicarbonate to compare the extent of reaction and reactivity to the RTI sorbent. A summary of the results is shown in Table 8.

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>RTI Supported Sorbent</th>
<th>Calcined SBC</th>
<th>Calcined Trona</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ removed (L) – adsorption</td>
<td>16.2</td>
<td>3.14</td>
<td>3.24</td>
</tr>
<tr>
<td>% CO₂ removal (max)</td>
<td>95</td>
<td>52</td>
<td>56</td>
</tr>
<tr>
<td>Time of adsorption (min)</td>
<td>6</td>
<td>1.5</td>
<td>1.8</td>
</tr>
<tr>
<td>Reactivity rate (mols/min)</td>
<td>0.258</td>
<td>0.133</td>
<td>0.164</td>
</tr>
</tbody>
</table>
Table 8 shows that RTI’s supported sorbent has a much higher reactivity rate and is able to remove higher percentages of CO₂ than the unsupported materials. The higher surface area of the supported material allows for more reactive sites to come in contact with CO₂ and leads to the observed performance enhancement. Although the unsupported materials have a higher theoretical capacity for CO₂ removal, they removed less than 60% of the CO₂ contained in the simulated flue gas over the life of the test. It is theorized that as the reaction takes place in these unsupported materials, the heat generated quickly raises the temperature of the sorbent particle and extinguishes the driving force for CO₂ adsorption. Despite the lower reactivity, the unsupported materials did absorb CO₂ in an entrained-bed reactor environment. Therefore, if better heat removal techniques (e.g., adding water for evaporative cooling) can be employed in this type of reactor design, their use may be feasible because of their relatively low raw material cost.

4.2 **Downflow Reactor Testing at RTI International**

Details of the experimental procedures used for downflow reactor testing are provided in Section 3.2.

**4.2.1 Downflow Testing with Supported Sorbents and Simulated Flue Gas**

A series of 15 downflow reactor tests was conducted with SCI-012705-1 sorbent, composed of 15% Na₂CO₃ supported on an inert ceramic material. A single test was then conducted with a newly manufactured batch of a supported sorbent (SCI-090905-1) prepared using the same recipe as for SCI-012705-1. The properties of this supported sorbent are shown in **Table 9**.

<table>
<thead>
<tr>
<th>Properties</th>
<th>SCI-012705-1 Sorbent</th>
<th>SCI-090905-1 Sorbent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compact Bulk Density (g/cc)</td>
<td>0.96</td>
<td>0.95</td>
</tr>
<tr>
<td>Average Particle Size (μm)</td>
<td>76.38</td>
<td>75.2</td>
</tr>
<tr>
<td>BET Surface Area (m²/g)</td>
<td>96.5</td>
<td>95.2</td>
</tr>
<tr>
<td>Attrition-resistance (DI)ⁿ</td>
<td>DI = 12.3</td>
<td>DI = 11.8</td>
</tr>
</tbody>
</table>

* RTI sorbents were characterized by the DI method. Lower DI values indicate physically strong catalysts and sorbents. A typical DI value range for Fluid Catalytic Cracking (FCC) Catalysts is 10–20.

The 16 supported sorbent tests were conducted at varying sorbent flow rates and temperatures. Gas flow rates were established before sorbent flow began. CO₂ concentration was monitored before, during, and after the period of sorbent flow. Test conditions and CO₂ removals are outlined in **Table 10**.
Table 10. Summary of Carbon Dioxide Removal Experiments in Laboratory Co-Current Downflow Reactor, Using RTI Supported Sorbent

<table>
<thead>
<tr>
<th>Experiment number</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
<th>13</th>
<th>14</th>
<th>15</th>
<th>16a</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ concentration [%]</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>2</td>
<td>1.5</td>
<td>10</td>
<td>10</td>
<td>15</td>
<td>15</td>
<td>15</td>
<td>15</td>
<td>15</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>Total gas flow [SLPM]</td>
<td>33</td>
<td>33</td>
<td>33</td>
<td>33</td>
<td>33</td>
<td>33</td>
<td>33</td>
<td>10</td>
<td>5</td>
<td>5</td>
<td>7.5</td>
<td>10</td>
<td>7.5</td>
<td>7.5</td>
<td>7.5</td>
<td>7.5</td>
</tr>
<tr>
<td>Temperature [°C]</td>
<td>60</td>
<td>62</td>
<td>56</td>
<td>60</td>
<td>34</td>
<td>25</td>
<td>27</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>40h</td>
<td>20</td>
<td>60h</td>
<td>20</td>
</tr>
<tr>
<td>Mass of sorbent used [g]</td>
<td>990</td>
<td>990</td>
<td>1961</td>
<td>4170</td>
<td>4374</td>
<td>4500</td>
<td>4600</td>
<td>4189.1</td>
<td>4009.8</td>
<td>3813.2</td>
<td>3783.4</td>
<td>3757.8</td>
<td>3742.2</td>
<td>3714.7</td>
<td>3672.3</td>
<td>10685.3</td>
</tr>
<tr>
<td>Achieved average sorbent flow rate [g/min]</td>
<td>33</td>
<td>33</td>
<td>53</td>
<td>139</td>
<td>162</td>
<td>225</td>
<td>92</td>
<td>202.5</td>
<td>225.9</td>
<td>169.6</td>
<td>245.1</td>
<td>214.3</td>
<td>189.5</td>
<td>178.2</td>
<td>174.2</td>
<td>195.8</td>
</tr>
<tr>
<td>Gas residence time in reactor [s]</td>
<td>12</td>
<td>12</td>
<td>12</td>
<td>12</td>
<td>12</td>
<td>12</td>
<td>12</td>
<td>41</td>
<td>82</td>
<td>82</td>
<td>56</td>
<td>41</td>
<td>56</td>
<td>56</td>
<td>56</td>
<td>56</td>
</tr>
<tr>
<td>Sorbent/CO₂ ratio [g/g]</td>
<td>16</td>
<td>16</td>
<td>25</td>
<td>66</td>
<td>76</td>
<td>159</td>
<td>87</td>
<td>101</td>
<td>224</td>
<td>111</td>
<td>110</td>
<td>73</td>
<td>85</td>
<td>80</td>
<td>78</td>
<td>88</td>
</tr>
<tr>
<td>Total gas/sorbent ratio [SLPM/LPM]</td>
<td>1000</td>
<td>1000</td>
<td>620</td>
<td>240</td>
<td>200</td>
<td>150</td>
<td>360</td>
<td>49.4</td>
<td>22.1</td>
<td>29.5</td>
<td>30.6</td>
<td>46.7</td>
<td>39.6</td>
<td>42.1</td>
<td>43.0</td>
<td>38.5</td>
</tr>
<tr>
<td>CO₂ loading on sorbent [wt% of sorbent]</td>
<td>1.2</td>
<td>1.0</td>
<td>1.2</td>
<td>.53</td>
<td>.68</td>
<td>.48</td>
<td>n/a</td>
<td>1.0</td>
<td>0.45</td>
<td>0.87</td>
<td>0.87</td>
<td>1.07</td>
<td>0.80</td>
<td>1.05</td>
<td>0.69</td>
<td>0.99</td>
</tr>
<tr>
<td>Steady-state CO₂ Removal [%]</td>
<td>19</td>
<td>16</td>
<td>29</td>
<td>35</td>
<td>52</td>
<td>76</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>Max. CO₂ removal rate [%]</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>67</td>
<td>97.4</td>
<td>100</td>
<td>96.8</td>
<td>96.0</td>
<td>78.7</td>
<td>82.7</td>
<td>84.0</td>
<td>53.9</td>
<td>87.2</td>
<td>n/a</td>
</tr>
</tbody>
</table>

n/a = not available

a New batch of RTI-5 sorbent (SCI-090905-1) used
b Sorbent was preheated to according temperature
c Based on sorbent relative bulk density of 1
The CO$_2$ concentration in the simulated flue gas leaving the downflow adsorber was measured during all co-current downflow tests. An example of the data collected during these tests appears in Figure 20, which is a plot of the data collected during Test #6. CO$_2$ removal data for all tests (shown in Table 10) were determined from the steady-state concentration differences before and during sorbent flow, as indicated by these plots.

![Figure 20. Carbon dioxide removal in downflow adsorption Test #6.](image)

The results of Test #6 indicate that significant CO$_2$ removal is possible in a 15-second gas residence time; however, gas residence times greater than 40 seconds are likely necessary to remove >90% of CO$_2$ from flue gas in this configuration. Table 10 shows that lower gas temperatures improve CO$_2$ removals, as previously confirmed in other reactor systems. One factor that may limit the rate of adsorption is localized heating of the sorbent particle surface. Although bulk sorbent temperatures are well within the temperature window for the bicarbonate reaction product, the particle surface may be warmer because of the exothermic reaction. Increasing sorbent-to-gas ratios decreases the potential effect of localized heating by providing a greater heat-sinking capacity. Greater sorbent loading also provides more active reaction sites for improved CO$_2$ removal.

Higher sorbent flow rates (higher solids-to-gas ratios) clearly improve CO$_2$ removal. Maximum CO$_2$ removals of >90% were observed in Tests #8–#11, with some of the highest sorbent-to-CO$_2$ ratios. Under favorable test conditions, capture of ≥90% was achievable for initial CO$_2$ concentrations of 10%
and 15% (representative of coal-fired flue gas). Full-scale downflow equipment (installed at a commercial power generation facility) would have a longer gas-solid contact time, which could lead to much greater CO₂ removal (and a greater extent of reaction). Gas-solid contact time can also be increased by using a modified adsorber design (i.e., an adsorber with staggered baffles, an adsorber with staggered screens, etc.).

4.2.2 Downflow Testing with Sodium Bicarbonate and Simulated Flue Gas

Three tests were conducted using calcined sodium bicarbonate (a mixture of Grade 3 and Grade 5) as the sorbent. Maximum CO₂ removals of between 57% and 91% were achieved. Test conditions and results are given in Table 11. Data for Test # 120505 are shown in Figure 21.

<table>
<thead>
<tr>
<th>Test</th>
<th>110205</th>
<th>110305</th>
<th>120505</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ Flow Rate (SLPM)</td>
<td>1.0</td>
<td>1.0</td>
<td>0.2</td>
</tr>
<tr>
<td>CO₂ Inlet Concentration (%)</td>
<td>10.7</td>
<td>10.7</td>
<td>10.8</td>
</tr>
<tr>
<td>H₂O Flow Rate (g/min)</td>
<td>0.79</td>
<td>0.79</td>
<td>0.15</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>~25</td>
<td>~25</td>
<td>~25</td>
</tr>
<tr>
<td>Average Sorbent Flow Rate (g/min)</td>
<td>299</td>
<td>160</td>
<td>250</td>
</tr>
<tr>
<td>Sorbent/CO₂ (g/g)</td>
<td>152</td>
<td>81</td>
<td>636</td>
</tr>
<tr>
<td>Maximum CO₂ Removal (%)</td>
<td>57</td>
<td>63</td>
<td>91</td>
</tr>
</tbody>
</table>

Figure 21. Carbon dioxide removal from simulated flue gas with calcined sodium bicarbonate in a co-current downflow adsorber: Test # 120505.

These low-temperature tests demonstrate that CO₂ can be readily removed from flue gas using low-cost (relative to engineered supported sorbents) calcined sodium bicarbonate. An economic
sensitivity analysis is required to determine the cost benefits and drawbacks of using sodium bicarbonate sorbent relative to the level of CO₂ capture desired.

4.3 Field Test of Heated Screw Conveyor Regeneration

Details of the experimental procedures used for field testing of heated screw conveyor regeneration are provided in Section 3.3.

4.3.1 Heat Transfer from Screw Conveyor to Supported Sorbent

Temperature measurements from the regeneration tests appear in Table 12.

Table 12. System Temperatures during Seven Decarbonation Tests

<table>
<thead>
<tr>
<th>Test number</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil set point temperature (deg. C)</td>
<td>149</td>
<td>149</td>
<td>149</td>
<td>149</td>
<td>149</td>
<td>149</td>
<td>166</td>
</tr>
<tr>
<td>Sorbent inlet temperature (deg. C)</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>49</td>
<td>50</td>
<td>50</td>
<td>55</td>
</tr>
<tr>
<td>Screw surface temperature (deg. C)</td>
<td>120</td>
<td>120</td>
<td>120</td>
<td>120</td>
<td>120</td>
<td>120</td>
<td>NA</td>
</tr>
<tr>
<td>Sorbent exit temperature (deg. C)</td>
<td>93</td>
<td>98</td>
<td>96.8</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Temp at first vent (approx. 1.5’)</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>90.2</td>
<td>90</td>
<td>93</td>
<td>95</td>
</tr>
<tr>
<td>Temp. at second vent (approx. 3’)</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>95</td>
<td>102</td>
<td>102</td>
<td>115</td>
</tr>
<tr>
<td>Temp. at third vent (approx. 4.5’)</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>115</td>
<td>117</td>
<td>117</td>
<td>123</td>
</tr>
</tbody>
</table>

NA = not measured

Table 12 demonstrates that heat transfer from the surface of the screw conveyor is adequate to heat the sorbent to the desired regeneration temperature of 120°C. In Tests #4, #5, #6, and #7, the sorbent temperature was measured at the entrance to the conveyor, at the first vent, at the second vent, and at the third vent. By the time the sorbent reached the third vent, its temperature was at least 115°C in all four tests and as high as 123°C in Test #7. These results are very encouraging and show that a heated screw conveyor at 120°C can transfer enough heat to heat the sorbent material to the desired regeneration temperature in roughly 3 minutes of sorbent residence time.

In addition to these promising results, there are several reasons to believe that the heated screw conveyor intended for the Dry Carbonate Process will be even more efficient at heating the sorbent than the test apparatus, including the following:

- The Dry Carbonate regeneration system will use a vertical screw conveyor. This will allow the sorbent to completely fill the empty spaces of the unit and will allow for better contact of the sorbent with all heated surfaces (i.e., the screw, other sorbent particles, and the entire surface of the jacket). In the horizontal configuration, heat transfer surfaces were limited to those of the screw flights.
The Dry Carbonate regeneration system does not require vent ports, which can readily allow heat to escape to the atmosphere.

- The Dry Carbonate regeneration system will be insulated, which will decrease heat loss.
- The Dry Carbonate regeneration system will use steam as the heating source rather than heated oil. Condensing steam has a better heat transfer coefficient than heated oil.

### 4.3.2 Mechanical Stability of Sorbent

The samples collected at Therma-flite were sent to RTI for particle size analysis using RTI’s Sympatec HELOS laser diffraction particle size analyzer. Particle size distributions are shown in Table 13. The samples were prescreened to eliminate particles >355 µm to ensure proper operation of the HELOS system. The percentage by weight of sorbent >355 µm for each sample is listed in Table 13 [under “>355µm (wt%)”]. Also listed in Table 13 are data from duplicate particle size analyses for each sample (columns labeled “1” and “2”). Ten percent of the sample weight is made up of particles with diameters less than or equal to the “x10” value given. (For example, for sample 100705a-PreTF, 10 wt% of the particles have a diameter of less than or equal to 44.9 µm.) Likewise, “x50” and “x90” represent the maximum particle size that includes 50% and 90% of the sample. Table 13 also lists the weight percentage of sorbent particles less than 21 µm and less than 42 µm in diameter.

### Table 13. Particle Size Analysis for Samples Taken During Therma-flite Tests

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Pass #</th>
<th>&gt;355 µm (wt %)</th>
<th>x10 (µm)</th>
<th>x50 (µm)</th>
<th>x90 (µm)</th>
<th>&lt;21 µm (%)</th>
<th>&lt;42 µm (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>1 2 1 2 1 2 1 2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100705a-PreTF</td>
<td>NA</td>
<td>0.72%</td>
<td>44.9 45.0</td>
<td>71.7 72.5</td>
<td>112.0 114.4</td>
<td>0.45 0.38</td>
<td>6.83 6.74</td>
</tr>
<tr>
<td>101205a-TF</td>
<td>1</td>
<td>1.12%</td>
<td>45.5 45.6</td>
<td>73.7 75.1</td>
<td>118.6 125.3</td>
<td>0.27 0.15</td>
<td>6.35 6.20</td>
</tr>
<tr>
<td>101205b-TF</td>
<td>1</td>
<td>1.11%</td>
<td>46.1 49.7</td>
<td>77.2 81.0</td>
<td>129.1 131.9</td>
<td>0.49 0.37</td>
<td>6.18 4.44</td>
</tr>
<tr>
<td>101205c-TF</td>
<td>1</td>
<td>1.08%</td>
<td>46.5 46.6</td>
<td>75.8 76.8</td>
<td>120.1 124.3</td>
<td>0.39 0.37</td>
<td>5.76 5.73</td>
</tr>
<tr>
<td>101205d-TF</td>
<td>2</td>
<td>3.10%</td>
<td>51.4 51.1</td>
<td>85.2 84.3</td>
<td>142.5 135.4</td>
<td>0.26 0.14</td>
<td>3.72 3.80</td>
</tr>
<tr>
<td>101205e-TF</td>
<td>2</td>
<td>2.16%</td>
<td>49.4 49.8</td>
<td>81.5 81.2</td>
<td>134.5 132.9</td>
<td>0.36 0.35</td>
<td>4.61 4.37</td>
</tr>
<tr>
<td>101205f-TF</td>
<td>3</td>
<td>1.70%</td>
<td>47.6 48.8</td>
<td>77.7 79.2</td>
<td>121.1 121.3</td>
<td>0.26 0.16</td>
<td>5.18 4.71</td>
</tr>
<tr>
<td>101205g-TF</td>
<td>3</td>
<td>2.14%</td>
<td>51.2 51.7</td>
<td>83.7 87.5</td>
<td>135.0 147.6</td>
<td>0.35 0.26</td>
<td>3.84 3.71</td>
</tr>
<tr>
<td>101205h-TF</td>
<td>4</td>
<td>1.90%</td>
<td>47.6 48.1</td>
<td>77.7 80.8</td>
<td>125.2 133.4</td>
<td>0.27 1.13</td>
<td>5.15 5.37</td>
</tr>
<tr>
<td>101205i-TF</td>
<td>9</td>
<td>1.96%</td>
<td>47.9 49.4</td>
<td>78.5 81.0</td>
<td>129.6 133.8</td>
<td>0.27 0.26</td>
<td>5.02 4.50</td>
</tr>
<tr>
<td>101205j-TF</td>
<td>14</td>
<td>3.50%</td>
<td>50.1 49.8</td>
<td>83.7 82.6</td>
<td>140.0 135.7</td>
<td>0.27 1.13</td>
<td>4.39 4.81</td>
</tr>
<tr>
<td>101205k-TF</td>
<td>24</td>
<td>1.62%</td>
<td>51.3 49.4</td>
<td>84.0 80.6</td>
<td>136.9 130.2</td>
<td>0.26 0.25</td>
<td>3.75 4.42</td>
</tr>
<tr>
<td>Averages</td>
<td></td>
<td>48.6 79.7 129.6</td>
<td>0.37 4.99</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
If attrition of the sorbent occurred during the Therma-flite tests, successive passes of the sorbent in the system would produce progressively smaller sorbent particles. It would be expected that particle sizes for x10, x50, and x90 would all decrease and that the percentage of material below 21 and 42 µm would increase. The data in Table 13 indicate that this is not the case. In fact, the x10, x50, and x90 particles sizes slightly increase, and the amount of material below 21 and 42 µm slightly decreases over successive passes of the sorbent. This minor increase is probably due to a slight agglomeration of the particles (due to the presence of water vapor after regeneration). These data suggest that there is little to no degradation of the sorbent over 24 passes in the screw conveyor system.

4.3.3 Extent of Sorbent Regeneration Determined by Thermogravimetric Analysis

Although it was established that the sorbent can be heated to the desired regeneration temperature, it is important to actually confirm that CO2 and H2O were released during the Therma-flite tests. TGA was used to measure the weight lost by collected samples upon heating. These samples were heated to 120°C and 160°C in an atmosphere of 100% N2. The samples tested include 100705a-PreTF (“fresh sample”), 101205a-TF (first bucket, first pass), 101205c-TF (third bucket, first pass), and 101205k-TF (24th pass). Figure 22 presents a comparison plot of the TGA results for these samples.

![Figure 22. TGA weight loss results for samples taken during Therma-flite testing.](image-url)
Figure 22 shows that the “fresh” sample (100705a-PreTF) has the greatest weight loss when heated. This is expected, since this sample should have the full amount of CO$_2$ and H$_2$O to release. Samples 101205a-TF and 101205c-TF, which represent the sorbent’s first pass through the heated screw conveyor, show a 2.5 wt% difference in weight loss as compared to the pretest sample. This suggests that CO$_2$ and H$_2$O were in fact released during the first pass through the system. However, comparative data for sample 101205k-TF (which represents the 24th pass through the system) prove that not all CO$_2$ and H$_2$O were removed in the first pass. The TGA plot for this sample shows a 4.1 wt% difference in weight loss as compared to the “fresh” sample. It would be expected that all CO$_2$ and H$_2$O would be removed by the 24th pass through the screw conveyor. However, the TGA plot for 101205k-TF shows a significant weight loss when the sample is heated to 120°C. It is suspected that this weight loss is due to water that was absorbed by the sorbent after it was tested, and that this weight loss does not represent loss of CO$_2$ that was on the sorbent before Therma-flite testing. To confirm this assumption, evolved gas mass spectroscopy was used to determine whether CO$_2$ was released upon heating of sample 101205k-TF.

### 4.3.4 Extent of Sorbent Regeneration Determined by Mass Spectroscopy

Figure 23 shows mass spectroscopy plots for samples 100705a-PreTF and 101205k-TF. The samples were heated to 120°C and 160°C, as in the TGA tests. The mass spectrometer was set to record CO$_2$ emitted by the samples as they were heated.

![Figure 23. Mass spectroscopy results for 100705a-PreTF and 101205k-TF.](image-url)
As shown in Figure 23, a significant amount of CO₂ was released (as expected) after heating of sample 100705a-PreTF. Sample 101205k-TF, however, released little to no CO₂ when heated. This suggests that all of the CO₂ was released during the Therma-flite tests (the sorbent was fully regenerated) and that the weight loss indicated by TGA testing is probably attributable to H₂O that was adsorbed after the field test.

4.4 Integrated Downflow Adsorber with Continuous Regeneration

Details of the experimental procedures used for integrated testing of the downflow adsorber and continuous regeneration are provided in Section 3.4.

4.4.1 Improvements to the Screw Conveyors to Enhance Sorbent Flow Rate Consistency

Flow distributors were added to the screw conveyors to improve the consistency of sorbent flow and prevent compaction and plugging of the sorbent. The screws were modified and tested individually.

4.4.1.1 Testing of the “Cooled” Screw Conveyor

The two screw conveyors were separated at the coupling, and a flow distributor was added at the inlet to the “cooled” screw. A sorbent feed hopper was temporarily mounted at the top of the coupling between the screws and filled with RTI’s supported sorbent (SCI-022806-1). Sorbent flow rate was determined gravimetrically by collecting the sorbent fed at a particular motor setting over a measured time period. Approximately 30 measurements were taken at each motor speed control setting. The average measured sorbent flow rates are shown in Figure 24.

A second flow distributor was added at the discharge from the regenerator screw, and the “cooled” screw flow rates were determined as described above. The flow rate characteristics of the “cooled” screw with both flow distributors installed is shown in Figure 25.

The installation of the first flow distributor (at the inlet point) improved the consistency of the sorbent flow versus previous observations during the shakedown testing of the integrated unit. The installation of the second flow distributor resulted in no noticeable difference in flow rate or flow consistency.
4.4.1.2 Testing of the "Heated" Screw Conveyor

A flow distributor was installed at the inlet to the “heated” screw conveyor, and sorbent flow rates through this screw were determined with the “cooled” screw disconnected. Sorbent was collected at
the coupling between the screws, and feed rates were determined gravimetrically over a measured time period. Average sorbent feed rates for different motor settings are shown in Figure 26.

As already mentioned, the installation of the flow distributors improved the consistency of the sorbent flow and eliminated most of the plugging problems. In addition, the results of the flow rate experiments for the operation of individual screws suggest that the motors should be operated at slightly different speeds (even though the motor capacities are identical) to match the flow rates of the two screws.

4.4.2 Heat Transfer Capability of the “Heated” Screw Conveyor

Several tests were conducted to determine the “heated” screw conveyor’s capacity to transfer heat to the sorbent particles. Sorbent temperature, measured at the outlet of the regenerator screw conveyor, is shown in Figure 27, as is a slight variation in steam pressure from the boiler that was observed.
The sorbent entered the regenerator screw conveyor at approximately 28°C and reached 100°C to 120°C under the noted process conditions. Steam pressure cycled between 43 and 50 psig. Previous research has shown that 120°C is the minimum temperature that should be attained for full sorbent regeneration. It is evidenced that the noted process conditions in this test can heat the sorbent close to 120°C, but additional steam pressure (higher saturation temperature) may be required to fully regenerate the sorbent.

4.4.3 Initial Carbon Dioxide Capture Tests with a Modified and Improved Integrated Unit

A test was conducted to observe the operation of the steam generator and sorbent regenerator of the modified and improved integrated system. Data from this test appear in Figure 28. During the test, CO₂ removal increased from about 28% to about 43% as the sorbent-to-gas ratio was increased. These low CO₂ removal efficiencies were assumed to have resulted from an incompletely regenerated sorbent. TGA testing confirmed this assumption, as test results showed an additional weight loss of about 5.5 wt% when the sorbent was heated to 150°C.
4.4.4 Testing Sorbent Regeneration to Improve Carbon Dioxide Adsorption in the Integrated System

It is likely that incomplete sorbent regeneration prevented the integrated system from achieving expected CO₂ capture levels in previous experiments. To test this theory, the integrated system was modified to mimic the conditions of the original downflow contactor, and several “downflow” tests were performed. Results from one of these tests can be seen in Figure 29, and a comparison of these data with those taken from the original contactor appears in Table 14.

At similar conditions (as in the downflow contactor), this experiment yielded about 80% CO₂ capture in the contactor. This is in contrast to the 50% CO₂ capture achieved in previous tests in the same contactor with the sorbent regenerated in the screw conveyor system. This experiment indicated that the regeneration of the sorbent in the integrated unit was inadequate to achieve the desired CO₂ capture. The regenerator operation must be improved. It is theorized that the integrated unit’s small laboratory boiler does not deliver the amount of steam required for full sorbent regeneration. It is anticipated that there will be plenty of steam available at the U.S. EPA’s field test site to remedy this issue of incomplete sorbent regeneration.
Figure 29. Carbon dioxide capture in modified integrated unit using sorbent calcined in a convection oven (screw conveyors not in operation).


<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ Concentration [%]</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Total Gas Flow [SLPM]</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Target Sorbent Flow [g/min]</td>
<td>200</td>
<td>200</td>
<td>200</td>
</tr>
<tr>
<td>Temperature [°C]</td>
<td>20</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Mass of Sorbent Used [g]</td>
<td>4189.1</td>
<td>7018.3</td>
<td>5509.5</td>
</tr>
<tr>
<td>Duration of Sorbent Flow [min:sec]</td>
<td>20:41</td>
<td>52:00</td>
<td>43:23</td>
</tr>
<tr>
<td>Achieved Sorbent Flow Rate [g/min]</td>
<td>202.5</td>
<td>135.0</td>
<td>127.0</td>
</tr>
<tr>
<td>Gas Residence Time in Reactor [s]</td>
<td>41</td>
<td>66.77</td>
<td>66.77</td>
</tr>
<tr>
<td>Sorbent/CO₂ Ratio [g/g]</td>
<td>101</td>
<td>68.76</td>
<td>64.70</td>
</tr>
<tr>
<td>CO₂ Loading on Sorbent [wt% of sorbent]</td>
<td>1</td>
<td>0.32</td>
<td>0.32</td>
</tr>
<tr>
<td>Maximum CO₂ Removal Rate [%]</td>
<td>97.40%</td>
<td>79.88%</td>
<td>81.19%</td>
</tr>
</tbody>
</table>

4.5 Performance and Exposure Testing of Sodium Carbonate–Based Sorbents Using Fossil-Derived Flue Gas

As described in Section 3.4, a continuous system was built and, after testing in RTI’s lab, installed at the EPA’s MPCRF to test the dry carbonate-based sorbent process using actual flue gas. The objectives of this phase of testing were as follows:
To demonstrate long-term continuous operation
To demonstrate continuous and complete regeneration
To examine the effects of real fossil fuel–derived flue gas on sorbent performance
To examine effects of continuous operation on sorbent attrition
To collect design data that will aid in scaling up the process

These particular goals are specific to the testing at the EPA research facility supplementing the broader goals of DOE as presented in DOE NETL’s 2007 Carbon Sequestration Technology Roadmap and Program Plan (http://www.netl.doe.gov/publications/carbon_seq/project%20portfolio/2007/2007Roadmap.pdf). Details of the experimental procedures used for testing RTI’s sodium carbonate-based sorbents using fossil-derived flue gas are provided in Section 3.5.

During testing at the U.S. EPA’s MPCRF, the sodium carbonate sorbent was exposed to fossil fuel–derived flue gas for approximately 230 hours. The sorbent was exposed to coal-derived flue gas for approximately 105 hours and to natural gas–derived flue gas for 125 hours. During testing, the sorbent underwent an estimated 116 cycles of adsorption and regeneration. At certain process conditions, >90% CO₂ capture was demonstrated for both natural gas–derived and coal-derived flue gas. A summary of the fossil fuel–derived flue gas tests appears in Table 15.

### 4.5.1 Demonstration of Continuous and Complete Regeneration

During the field test at EPA, the extent of regeneration of the sorbent was improved over that observed during shakedown and testing in the laboratory. Although the 3 kW electric boiler, described in Section 3.4, provided steam of adequate temperature and pressure, it could not provide an adequate volume (or amount) of steam for sorbent regeneration. To test this theory, steam was supplied by EPA’s 80 psig steam header rather than by the small boiler. The temperature of the steam from the 80 psig header was relatively constant at 150°–160°C. A comparison of the regeneration parameters appears in Figure 30.
### Table 15. Summary of Fossil Fuel–Derived Flue Gas Testing at EPA’s MPCRF

<table>
<thead>
<tr>
<th>Date</th>
<th>Fuel</th>
<th>On-Stream Time</th>
<th>Flow Rate (SCFH)</th>
<th>Average CO₂ Capture (%)</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>2/28/2007</td>
<td>Nat. Gas</td>
<td>45 min</td>
<td>42</td>
<td>84.2</td>
<td>Initial Test for Shakedown</td>
</tr>
<tr>
<td>3/12/2007</td>
<td>Nat. Gas</td>
<td>41 min</td>
<td>30</td>
<td>75.4</td>
<td></td>
</tr>
<tr>
<td>3/13/2007</td>
<td>Nat. Gas</td>
<td>9.5 hrs</td>
<td>25</td>
<td>87.6</td>
<td></td>
</tr>
<tr>
<td>3/14/2007</td>
<td>Nat. Gas</td>
<td>24 hrs</td>
<td>20</td>
<td>98.5</td>
<td></td>
</tr>
<tr>
<td>3/15/2007</td>
<td>Nat. Gas</td>
<td>22.5 hrs</td>
<td>40</td>
<td>80.2</td>
<td></td>
</tr>
<tr>
<td>3/22/2007</td>
<td>Nat. Gas</td>
<td>3.5 hrs</td>
<td>35</td>
<td>N/A</td>
<td>Did not Regenerate During Test</td>
</tr>
<tr>
<td>3/23/2007</td>
<td>Coal</td>
<td>4 hrs</td>
<td>25</td>
<td>77.0</td>
<td>Eastern Bituminous Med. Sulfur Coal</td>
</tr>
<tr>
<td>3/25/2007</td>
<td>Coal</td>
<td>15.5 hrs</td>
<td>25</td>
<td>92.5</td>
<td>Eastern Bituminous Med. Sulfur Coal Lost Flue Gas Flow In Middle of Run</td>
</tr>
<tr>
<td>3/27/2007</td>
<td>Nat. Gas</td>
<td>1.5 hrs</td>
<td>30</td>
<td>96.1</td>
<td></td>
</tr>
<tr>
<td>3/28/2007</td>
<td>Coal</td>
<td>20.5 hrs</td>
<td>Variable</td>
<td>N/A</td>
<td>60% PRB&lt;sup&gt;a&lt;/sup&gt; mixed with 40% East. Bit. Coal Erratic Flow Due to Pumping Issues</td>
</tr>
<tr>
<td>3/29/2007</td>
<td>Nat. Gas</td>
<td>16.5 hrs</td>
<td>30</td>
<td>72.4</td>
<td></td>
</tr>
<tr>
<td>3/30/2007</td>
<td>Coal</td>
<td>21 Hrs</td>
<td>30</td>
<td>N/A</td>
<td>70% PRB mixed with 30% East. Bit. Coal Erratic Flow Due to Combustor Problems</td>
</tr>
<tr>
<td>5/6/2007</td>
<td>Coal</td>
<td>20.5 hrs</td>
<td>40</td>
<td>Variable</td>
<td>80% PRB mixed with 20% East. Bit. Coal Varied Sorbent Flow</td>
</tr>
<tr>
<td>5/7/2007</td>
<td>Nat. Gas</td>
<td>4.5 hrs</td>
<td>40</td>
<td>Variable</td>
<td>Lost Flow During Overnight Hours</td>
</tr>
<tr>
<td>5/8/2007</td>
<td>Coal</td>
<td>22 hrs</td>
<td>40</td>
<td>Variable</td>
<td>90% PRB mixed with 10% East. Bit. Coal Varied Sorbent Flow</td>
</tr>
<tr>
<td>5/10/2007</td>
<td>Nat. Gas</td>
<td>19 hrs</td>
<td>80</td>
<td>Variable</td>
<td>Varied Sorbent Flow</td>
</tr>
<tr>
<td>5/11/2007</td>
<td>Nat. Gas</td>
<td>5 hrs</td>
<td>40</td>
<td>95.0</td>
<td></td>
</tr>
</tbody>
</table>

Total Time on Stream with Nat. Gas: 128 hrs
Total Time on Stream with Coal: 104 hrs

Estimated Total Number of Adsorption/Regeneration Cycles (only includes tests using fossil fuel–derived flue gas, excludes simulated flue gas testing): 116

---

<sup>a</sup> PRB = Powder River Basin coal
<sup>b</sup> SCFH = standard cubic feet per hour
As shown in Figure 30, the sorbent temperature required for complete regeneration could not be reached using steam provided by the small electric boiler. To obtain an accurate comparison, the boiler steam pressure set point was 80 psig, although the pressure never exceeded 74 psig. Figure 30 clearly shows that steam temperatures from the boiler and the header are comparable; however, because of the inadequate amount of steam produced by the small boiler, the regeneration temperature never reached the levels desirable for full regeneration of the sorbent. The electric boiler typically resulted in regeneration temperatures of approximately 116°C. At very low sorbent flow rates, the boiler produced enough steam to achieve a regeneration temperature as high as 125°C (a favorable temperature for regeneration). Given the sorbent residence time in the regenerator, temperatures of 140°–150°C were necessary to produce more complete CO₂ capture.

Even with regeneration temperatures as high as 140°–150°C, the sorbent residence time in the regenerator proved to be important in determining the CO₂ capture. It is reasonable to expect that a higher sorbent flow rate along, with a fixed gas flow of a given CO₂ concentration, would result in a higher level of CO₂ capture. However, the higher sorbent flow rate resulted in a lower sorbent residence time in the...
regenerator, leading to reduced regeneration and, therefore, lower capture efficiency. A parametric test performed using simulated flue gas supports this explanation. Figure 31 shows the CO₂ concentration in the adsorber exit gas as a function of sorbent flow rates. At 84 lb/hr (the highest possible sorbent flow), CO₂ capture decreases and levels off. This is most likely the result of incomplete regeneration caused by a shorter residence time in the regenerator. It is estimated that the residence time in the regenerator is 1.6 hr at 36 lb/hr, 50 minutes for 72 lb/hr, and 40 minutes for 84 lb/hr sorbent flow rates. The data suggest that a residence time of approximately 1 hr is required for a full regeneration at 150°C.

![Figure 31. Parametric testing to observe effects of sorbent flow and regeneration residence time on carbon dioxide capture.](image)

### 4.5.2 Evaluation of Sorbent Performance after Exposure to Fossil Fuel–Derived Flue Gas

One of the primary objectives of using coal-fired flue gas to test the CO₂ capture system and sorbent was to examine the effects contaminants in the coal-derived flue gas may have on the sorbent material. As discussed previously, a permanent deactivation was expected of some the active sites of the sorbent material, resulting from an irreversible reaction between sodium carbonate in the sorbent and hydrogen chloride and sulfur dioxide present in the coal flue gas. Initial testing at EPA during the installation of their lime slurry scrubber indicated that the sulfur concentration of the flue gas exiting the
scrubber was 15–20 ppm SO₂ while burning low-sulfur bituminous coal. Additionally, very low levels of HCl were expected in the flue gas downstream of the scrubber. No measurements were taken for the HCl concentration before testing.

Even though it was anticipated that some of the active sites would be poisoned by SO₂ and HCl, the low concentrations of these contaminants were expected to cause minimal deterioration to the sorbent activity. When the CO₂ capture rate was measured before and after exposure to coal-derived flue gas, the data indicate little to no deactivation. In fact, the performance appears to have improved over time. This may be attributable to inconsistencies in sorbent flow rates, varying extents of regeneration, differences in moisture content, or other unknown factors. **Figure 32** compares the CO₂ capture before and after exposure to coal-derived flue gas (flue gas flowing at 40 SCFH, and screw drive motor control frequency at 20 Hz, corresponding to 72 lb sorbent /hr). The test gas was natural gas–derived flue gas. The test performed on 03/15/2007 took place before any the sorbent was exposed to coal-derived flue gas. The test performed on 05/11/2007 took place after 104 hours of exposure to coal-derived flue gas.

![Figure 32. Comparison of carbon dioxide capture before and after exposure to coal-derived flue gas.](attachment:image.png)
TGA data collected to corroborate the integrated system data shown in Figure 32 are contradictory. **Figure 33** compares results of a test performed with a relatively fresh sorbent sample with those of a test of a sorbent sample removed from the integrated system on 04/26/2007 after 61 hours of coal-derived flue gas exposure. The relatively fresh sample came from the same production batch but was exposed to only a few cycles of adsorption/regeneration during early lab testing using simulated flue gas. Figure 33 shows a difference of 1.7 wt% in the mass of material absorbed by the sorbent.

![TGA plot comparing weight gain of adsorption reaction for fresh and coal flue gas–exposed sorbents.]

**Figure 33.** TGA plot comparing weight gain of adsorption reaction for fresh and coal flue gas–exposed sorbents.

**Figure 34** suggests that the sorbent had deactivated as a result of exposure to coal-derived flue gas. However, when the TGA data for the sorbent withdrawn from the integrated system on 04/26/2007 are compared to those from a similar TGA experiment, the data do not suggest such a high degree of deactivation. The plot in Figure 34 illustrates this point. A TGA experiment using the same conditions, without introducing CO₂, produced nearly identical results.
Comparison of the two plots suggests that the difference in weight loss is purely from changes in the sorbent’s ability to absorb water vapor. Nearly identical results obtained both with and without CO₂ in the gas matrix indicate that the sorbent has changed, though it is not clear that there has been any decrease in sorbent reactivity. The difference between the sorbent samples appears to the result of reduced moisture pickup by the exposure sorbent, which could be due to attrition, loss of surface area, or loss of pore volume. Measurements of the pore volume and surface area of the sorbent samples support this. The sorbent did experience a decrease in surface area, porosity, and density over the course of testing. Table 16 lists sorbent characteristics before and after exposure to fossil fuel–derived flue gases (and several hundred cycles of adsorption and regeneration).

**Table 16. Sorbent Characteristics Before and After Exposure to Fossil Fuel–Derived Flue Gases and Several Hundred Cycles of Adsorption/Regeneration**

<table>
<thead>
<tr>
<th></th>
<th>Before Exposure</th>
<th>After Exposure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface Area [m²/g]</td>
<td>106.4</td>
<td>93.5</td>
</tr>
<tr>
<td>Total Pore Area [m²/g]</td>
<td>160.0</td>
<td>127.6</td>
</tr>
<tr>
<td>Bulk Density [g/mL]</td>
<td>1.45</td>
<td>1.02</td>
</tr>
<tr>
<td>Porosity [%]</td>
<td>47.39</td>
<td>36.8</td>
</tr>
</tbody>
</table>
After the experiments were complete, an elemental analysis was performed on the sorbent using an inductively coupled plasma atomic emission spectrometer (ICP-AES) to determine how the sample was affected. The analysis focused on determining the content of aluminum, sodium, sulfur, mercury, and arsenic in the sorbent. Mercury and arsenic measurements were below the detection limit of 500 ppm. Similarly, the amount of sulfur was also below 500 ppm. One interesting finding was a change in the sodium content, possibly indicating a loss of the active carbonate material. ICP-AES testing showed that the amount of sodium in the sorbent sample decreased by about 25%. The results of the aluminum (Al), sodium (Na), and sulfur (S) tests are outlined in Table 17.

Table 17. Results of Elemental Analysis of New and Used Sorbent Using ICP-AES

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Na (%Wt)</th>
<th>Al (%Wt)</th>
<th>S (µg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>New Sorbent</td>
<td>4.07</td>
<td>39.0</td>
<td>&lt;500</td>
</tr>
<tr>
<td>New Sorbent Duplicate</td>
<td>4.37</td>
<td>37.5</td>
<td>&lt;500</td>
</tr>
<tr>
<td>Used Sorbent</td>
<td>3.04</td>
<td>37.1</td>
<td>&lt;600</td>
</tr>
<tr>
<td>Used Sorbent Duplicate</td>
<td>3.17</td>
<td>36.8</td>
<td>&lt;500</td>
</tr>
</tbody>
</table>

High resolution micrographs of both the new and tested sorbent were made using a scanning electron microscope (SEM) to see whether any distinct visible changes occurred over the course of exposure testing. Figures 35 and 36 are micrographs showing the surface of a sorbent particle before and after the exposure tests.
The micrographs show that the sorbent particles underwent a physical change over the course of the experimental program. The surface of the exposed sorbent particle appears “fuzzy” in comparison with that of the new sorbent.

### 4.5.3 Effects of Long-Term Testing on Sorbent Attrition

The 15 wt% sodium carbonate on alumina produced by Süd Chemie, Inc., labeled SCI-022806 was introduced to the bench scale CO₂ capture unit on 03/30/2006. This single charge of sorbent was used for initial shakedown testing as well as all long-term fossil fuel–derived flue gas exposure testing at the EPA’s MPCRF. Testing was concluded on 05/10/2007. During the 14 months of shakedown and testing, the sorbent was circulated for about one thousand hours and underwent several hundred cycles of adsorption and regeneration. Some degree of attrition was expected to result from mechanical stress.

To investigate the sorbent’s attrition, average particle size was measured before the sorbent was added to the system and then again after all tests were complete. Although this can indicate attrition resistance, the data should not be taken at face value. Many of the fines generated as the sorbent circulated were entrained in the exhaust gas and carried out of the system. Without the fines in the particle size analysis sample, the data indicate an increase in the average particle size. The average particle size before loading the sorbent into the system was 63.8 microns. The average particle size of the sorbent after...
all tests were complete was 95.0 microns. Fines collected from the sample filter had an average particle size of 12.2 microns.

In addition to the particle size measurements, an SEM micrograph shows that the sorbent did undergo some degree of physical attrition. Although it does not quantify the extent of attrition, it provides useful insight into the strength of the sorbent. There are many large, spherical particles, but there are also many small fragments, which may or may not be fragments of sorbent particles. After 14 months of testing, foreign particles may have contaminated the sorbent charge. Figures 37 and 38 are lower-magnification SEM micrographs of sorbent particles.

![Figure 37. SEM micrograph of new, unexposed sorbent particles.](image)
4.5.4 Overall Testing Performance and Scale-Up Data

As stated in Section 3.5, the bench-scale CO₂ capture unit was tested for a total of 230 hours with both natural gas– and coal-derived flue gases. These tests performed at various process conditions yielded information useful in the scale-up of the process, such as sorbent loading per pass, ideal gas residence time, and sorbent-to-gas ratios. **Table 18** presents the major data taken from the fossil fuel–derived flue gas tests.

One of the most important insights gained from this data is that the sorbent loading per pass should be increased to improve process economics. The data indicate that, on average, the sorbent loading per pass is around 5% of the theoretical stoichiometric loading. Further development should include a more direct focus on increasing sorbent loading. This will reduce the energy needed to heat the unreacted material and the inert support, thus improving the overall economics of the process.

The data also indicate that, as residence time increases, increasing the sorbent-to-gas ratio has less of an effect on CO₂ capture, and thus decreases efficiency. **Figure 39** shows that as the residence time decreases, the CO₂ capture decreases, thus requiring a greater amount of sorbent to capture a given amount of CO₂.

![Figure 38. SEM micrograph of used, exposed sorbent particles after 14 months of testing.](image-url)
## Table 18. Data Summary of Fossil Fuel–Derived Flue Gas Runs

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Gas Flow Rate (SCFH)</th>
<th>Sorbent Flow Rate (lb/hr)</th>
<th>lb CO2 introduced/lb active ingredient</th>
<th>lb CO2 captured/lb active ingredient</th>
<th>mole CO2 captured/mole active ingredient</th>
<th>CO2 Removed (%)</th>
<th>Gas Residence Time (s)</th>
<th>Total Sorbent/CO2 captured (lb/lb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nat. Gas</td>
<td>30</td>
<td>36</td>
<td>0.0290</td>
<td>0.0220</td>
<td>0.0530</td>
<td>75.4</td>
<td>39</td>
<td>229</td>
</tr>
<tr>
<td>Nat. Gas</td>
<td>25</td>
<td>72</td>
<td>0.0102</td>
<td>0.0089</td>
<td>0.0214</td>
<td>87.6</td>
<td>46</td>
<td>657</td>
</tr>
<tr>
<td>Nat. Gas</td>
<td>20</td>
<td>72</td>
<td>0.0114</td>
<td>0.0113</td>
<td>0.0272</td>
<td>98.5</td>
<td>55</td>
<td>583</td>
</tr>
<tr>
<td>Nat. Gas</td>
<td>40</td>
<td>72</td>
<td>0.0194</td>
<td>0.0155</td>
<td>0.0373</td>
<td>80.2</td>
<td>31</td>
<td>345</td>
</tr>
<tr>
<td>Coal</td>
<td>20</td>
<td>72</td>
<td>0.0163</td>
<td>0.0125</td>
<td>0.0301</td>
<td>76.8</td>
<td>55</td>
<td>533</td>
</tr>
<tr>
<td>Coal</td>
<td>25</td>
<td>36</td>
<td>0.0438</td>
<td>0.0406</td>
<td>0.0978</td>
<td>92.5</td>
<td>46</td>
<td>164</td>
</tr>
<tr>
<td>Nat. Gas</td>
<td>30</td>
<td>72</td>
<td>0.0144</td>
<td>0.0138</td>
<td>0.0332</td>
<td>96.1</td>
<td>39</td>
<td>483</td>
</tr>
<tr>
<td>Nat. Gas</td>
<td>30</td>
<td>72</td>
<td>0.0336</td>
<td>0.0279</td>
<td>0.0672</td>
<td>83.0</td>
<td>39</td>
<td>239</td>
</tr>
<tr>
<td>Nat. Gas</td>
<td>40</td>
<td>72</td>
<td>0.0537</td>
<td>0.0318</td>
<td>0.0766</td>
<td>59.2</td>
<td>31</td>
<td>210</td>
</tr>
<tr>
<td>Nat. Gas</td>
<td>40</td>
<td>84</td>
<td>0.0460</td>
<td>0.0303</td>
<td>0.0730</td>
<td>65.8</td>
<td>31</td>
<td>220</td>
</tr>
<tr>
<td>Nat. Gas</td>
<td>40</td>
<td>36</td>
<td>0.1024</td>
<td>0.0348</td>
<td>0.0838</td>
<td>34.0</td>
<td>31</td>
<td>191</td>
</tr>
<tr>
<td>Nat. Gas</td>
<td>40</td>
<td>54</td>
<td>0.0683</td>
<td>0.0402</td>
<td>0.0968</td>
<td>58.9</td>
<td>31</td>
<td>166</td>
</tr>
<tr>
<td>Nat. Gas</td>
<td>40</td>
<td>84</td>
<td>0.0439</td>
<td>0.0289</td>
<td>0.0696</td>
<td>65.9</td>
<td>31</td>
<td>230</td>
</tr>
<tr>
<td>Nat. Gas</td>
<td>80</td>
<td>36</td>
<td>0.1065</td>
<td>0.0213</td>
<td>0.0513</td>
<td>20.0</td>
<td>16</td>
<td>313</td>
</tr>
<tr>
<td>Nat. Gas</td>
<td>80</td>
<td>54</td>
<td>0.0710</td>
<td>0.0159</td>
<td>0.0383</td>
<td>22.4</td>
<td>16</td>
<td>419</td>
</tr>
<tr>
<td>Nat. Gas</td>
<td>80</td>
<td>72</td>
<td>0.0533</td>
<td>0.0143</td>
<td>0.0345</td>
<td>26.8</td>
<td>16</td>
<td>468</td>
</tr>
<tr>
<td>Nat. Gas</td>
<td>40</td>
<td>72</td>
<td>0.0226</td>
<td>0.0215</td>
<td>0.0518</td>
<td>95.0</td>
<td>30</td>
<td>310</td>
</tr>
</tbody>
</table>
4.6 Effects of Flue Gas Contaminants on a Sodium Carbonate Sorbent

Details of the experimental procedures used for testing the effects of flue gas contaminants on a sodium carbonate-based sorbent are provided in Section 3.6.

4.6.1 Reactions of Sulfur Dioxide with Sodium Carbonate Sorbent

4.6.1.1 LSU Electrobalance (TGA) Studies

A series of tests to determine the extent and reversibility of reactions between Na₂CO₃ sorbents and SO₂ contaminants expected to be present in flue gas was conducted at LSU, under subcontract to RTI. Figure 40 shows electrobalance data for a three-cycle test in which a simulated flue gas containing 0.2% SO₂, 8% CO₂, 16% H₂O, and balance He (no O₂) was used. The initial calcination progressed as expected, with a final dimensionless weight very near the theoretical value of 0.63. The dimensionless weight increased rapidly during the first carbonation cycle and reached a maximum of about 0.88 approximately 100 minutes later. The dimensionless weight then began to decrease to about 0.83, and the carbonation cycle was ended. After the second calcination cycle, the final dimensionless weight only decreased to
0.68. In the second carbonation cycle, the maximum dimensionless weight was only about 0.82. The minimum weight following the third calcination was 0.71, and the maximum weight at the end of the third carbonation was 0.78. When the sorbent was calcined for a fourth time, the final weight was only about 0.74. The calcination temperature was then increased stepwise to 200°C. Little, if any, additional weight loss occurred at these higher temperatures. These results suggest the formation of increasing amounts of Na₂SO₃ during each carbonation cycle. Further, it appears that the Na₂SO₃ is stable in He at temperatures as high as 200°C.

The cause of the maximum in the dimensionless weight, which occurred only during the first carbonation cycle, is unknown. The amount of CO₂ removed in each cycle is proportional to the difference in dimensionless weight at the end of the carbonation and subsequent calcination cycles. The difference decreased from 0.15 in cycle 1 (based on the final dimensionless weight of 0.83) to 0.11 in cycle 2 and 0.04 in cycle 3. Clearly, after these cycles, there is little CO₂ removal capacity in the sorbent.

Decreasing the SO₂ concentration in the carbonation gas to 0.1% produced qualitatively similar results, as is shown in Figure 41; however, the reduction in CO₂ capacity occurred at a slower rate, thus allowing five cycles to be completed. Note that no dimensionless weight maxima were observed during any of the carbonation cycles shown in Figure 41. The difference in dimensionless weight at the end of carbonation cycle 1 and calcination cycle 2 was about 0.17. At the end of four cycles, this difference decreased to 0.06. These numbers suggest that the loss in CO₂ capacity following three cycles with 0.2%
SO₂ in the feed gas was almost 75%, compared to an approximate 65% loss following four cycles with 0.1% SO₂ in the feed gas.

![Figure 41. Dimensionless weight of sodium bicarbonate #3 versus time showing the effect of 0.1% sulfur dioxide in the carbonation gas.](image)

Results of a test using calcined trona as the sorbent with 0.1% SO₂ in the carbonation gas were qualitatively similar to those for sodium carbonate grade #3, as shown in Figure 42. Both O₂ and SO₂ were added to the carbonation gas in this test. This figure shows a five-cycle test using trona with 0.1% SO₂ and 2.0% O₂ added to the carbonation gas. The loss in CO₂ capacity (again, measured by the loss in dimensionless weight after carbonation) was also about 65% after four cycles.

These data suggest that the reaction between the sorbent and SO₂ in flue gas would be rapid and, under the expected process conditions, irreversible. Although the expected application for the Dry Carbonate Process is treatment of flue gas after wet flue gas desulfurization (WFGD), it is clear that the sulfur remaining after 90%+ removal will necessitate periodic sorbent replacement. In any case, periodic sorbent makeup would be necessary to compensate for losses due to attrition.
4.6.1.2 Results of RTI Fluid Bed Testing

Essentially all of the SO₂ input to the reactor was absorbed by the sorbent. Except for a few gas chromatography (GC) samples that showed trace concentrations (3–20 ppmv) of SO₂, all samples (from both carbonation and desorption cycles) were below the detection limit of the GC, which was about 3 ppmv. CO₂ removals obtained during the carbonation cycles were typically 10% to 20%, as determined by GC analyses of the reactor outlet gas. In conclusion, SO₂ at concentrations in the range of those expected in desulfurized flue gas was essentially completely removed. SO₂ was not released from the sorbent to any appreciable extent at 140°C.

4.6.2 Reactions of Hydrogen Chloride with Sodium Carbonate Sorbent

Greater than 98% of the inlet HCl was removed, and this removal rate was observed both with and without the addition of 5.6% water vapor. This removal rate was maintained for approximately 80 minutes. The sorbent bed was regenerated with dry nitrogen at 150°C and subjected to a second carbonation cycle. HCl removals in the second cycle consistently exceeded 99%.

4.6.3 Mercury Sorption Testing with a Sodium Carbonate Sorbent

Three different sorbent formulations were tested in the small-scale screening apparatus: 20% Na₂CO₃ on alumina, 40% Na₂CO₃ on alumina, and 20% Na₂CO₃ on a silica-containing support. No detectable Hg collection occurred on the alumina-supported materials. The silica-containing material did show a small capture efficiency (approximately 10% of the Hg in the challenge gas).
This work indicates that Hg will not be trapped in the most likely sorbent formulations (e.g., alumina-supported materials). Thus, this sorbent cannot be used as a polishing step for Hg removal from flue gas.

5.0 Economic Evaluation

To evaluate the commercialization potential of the Dry Carbonate Process, cost estimates were developed on the basis of 90% removal of the CO₂ produced by a coal-fired boiler with a capacity of 500 MWₑ (nominal). The DOE’s Carbon Capture and Sequestration Systems Analysis Guidelines (http://www.netl.doe.gov/technologies/carbon_seq/Resources/Analysis/pubs/CO2CaptureGuidelines.pdf) were used in evaluating the economic performance of the Dry Carbonate Process. These guidelines also served as a reference for comparing the Dry Carbonate Process to both a pulverized coal (PC)-fired power plant implementing an MEA system for CO₂ capture and a power plant without CO₂ capture. With the equipment and utility streams sized accordingly for the Dry Carbonate Process, estimates of the power performance, operating costs, and capital costs were made. The capacity in a plant using dry carbonate CO₂ capture is 349 MWₑ after considering all auxiliary power loads and heat integration for the entire power cycle. Such a plant operates with an estimated higher heating value (HHV) efficiency of 30.6% compared to 40.5% for a plant with no CO₂ capture technology. Annual operating costs for the entire power plant were estimated to be approximately $71 million (3.5 ¢/kWh), representing a $16.7 million (1.47 ¢/kWh) increase over the baseline power plant operating cost. Capital costs were estimated at $60 million for the dry carbonate CO₂ removal and compression system and $483 million for the entire plant. This is less expensive than the MEA capture and compression system, which has an estimated capital cost of $114 million and total plant cost of $532 million. The baseline power plant has a capital cost of $434 million. In terms of overall COE, a power plant implementing the Dry Carbonate Process for CO₂ removal has a COE of 8.1 ¢/kWh, while a plant with no CO₂ capture has a COE of 5.5 ¢/kWh. Therefore, a plant that uses the Dry Carbonate Process to remove CO₂ will incur a 48% increase in the COE provided to customers. This estimated cost increase is higher than DOE targets of limiting COE increase to 35%, but the Dry Carbonate Process is significantly lower in cost and more energy efficient than conventional MEA technology (Note: these are DOE-NETL’s 2008 cost targets for CO₂ capture technologies as provided in the DOE-NETL’s Carbon Sequestration Technology Roadmap and Program Plan – the latest version of this document being the 2007 publication (http://www.netl.doe.gov/publications/carbon_seq/ project%20portfolio/2007/2007Roadmap.pdf)). At present, the studies show the Dry Carbonate Process to be 10% better than the MEA capture process on a ¢/kWh basis.
5.1 Power Performance

5.1.1 Pulverized Coal Power Plant with No Carbon Dioxide Removal

The PC power plant with no CO₂ removal is described in the 2000 Electrical Power Research Institute (EPRI) report *Evaluation of Innovative Fossil Fuel Power Plants with CO₂ Removal* (EPRI, 2000). The study conducted on this power plant was referred to as Case 7C. Case 7C takes a market-based design approach, and the plant configuration reflects the information and design practices that were current at the time of the EPRI study. A once-through steam generator is used in this case to power a double-reheat supercritical steam turbine. Also, wet limestone flue gas desulfurization (FGD) is used to limit SO₂ emissions. These design assumptions were also used for the power plants in the MEA system case and the Dry Carbonate Process case. Additional assumptions used for power performance and economic analyses are listed in Table 19.

5.1.2 Pulverized Coal Power Plant with Carbon Dioxide Removal (MEA)

The PC power plant with an MEA system for CO₂ capture is also described in the 2000 EPRI report and is referred to as Case 7A. The coal-fired flue gas of Case 7A is routed to an inhibited MEA adsorber-stripper system following wet limestone FGD. The MEA solution removes 90% of the CO₂ present in the flue gas. After adsorption, low-pressure steam is used to strip CO₂ and to regenerate the absorbent. The CO₂ is then compressed to supercritical conditions. Additional design assumptions are provided in Table 19.

5.1.3 Pulverized Coal Power Plant with Carbon Dioxide Removal (Dry Carbonate Process)

The theoretical PC power plant using the Dry Carbonate Process for CO₂ capture is described in Section 1.0 of this report. After wet FGD, the coal-fired flue gas enters the entrained-flow contactor of the Dry Carbonate Process. Ninety percent of the CO₂ contained in this flue gas is removed by a carbonate-based sorbent. The sorbent is regenerated (and CO₂ and water subsequently released) using low-pressure steam from the power plant cycle. Water is condensed from the regeneration gas stream, leaving pure CO₂. The CO₂ is then compressed to supercritical conditions. Additional design assumptions are provided in Table 19.

5.1.4 Assumptions and Analysis Design Basis

Table 19 presents the general assumptions and design basis used to evaluate the power performance, operating costs, and capital costs of all three PC plant cases.
Table 19. Supercritical Pulverized Coal Plant (with and without carbon dioxide capture) Assumptions and Analysis Design Basis (all dollar values are in 2005 dollars)

<table>
<thead>
<tr>
<th></th>
<th>Case 7C</th>
<th>Case 7A</th>
<th>Dry Carbonate Case</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Location</strong></td>
<td>East-West Region</td>
<td>East-West Region</td>
<td>East-West Region</td>
</tr>
<tr>
<td><strong>Fuel</strong></td>
<td>Illinois #6 Coal</td>
<td>Illinois #6 Coal</td>
<td>Illinois #6 Coal</td>
</tr>
<tr>
<td><strong>Delivered Cost of Fuel ($/MM Btu)</strong></td>
<td>$1.26/MM Btu</td>
<td>$1.26/MM Btu</td>
<td>$1.26/MM Btu</td>
</tr>
<tr>
<td><strong>Design/Construction Period (years)</strong></td>
<td>4 years</td>
<td>4 years</td>
<td>4 years</td>
</tr>
<tr>
<td><strong>Plant Start-Up Date</strong></td>
<td>Jan-05</td>
<td>Jan-05</td>
<td>Jan-05</td>
</tr>
<tr>
<td><strong>Land Area/Unit Cost ($/acre)</strong></td>
<td>$1,631/acre</td>
<td>$1,631/acre</td>
<td>$1,631/acre</td>
</tr>
<tr>
<td><strong>Capital Cost Year Dollars</strong></td>
<td>2005</td>
<td>2005</td>
<td>2005</td>
</tr>
<tr>
<td><strong>Capacity Factor (%)</strong></td>
<td>65%</td>
<td>65%</td>
<td>65%</td>
</tr>
<tr>
<td><strong>Levelized Capital Charge Factor (%)</strong></td>
<td>14%</td>
<td>14%</td>
<td>14%</td>
</tr>
<tr>
<td><strong>Project Book Life</strong></td>
<td>20 years</td>
<td>20 years</td>
<td>20 years</td>
</tr>
<tr>
<td><strong>Engineering Fees</strong></td>
<td>6%</td>
<td>6%</td>
<td>6%</td>
</tr>
<tr>
<td><strong>Process Contingency - Most plant components</strong></td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
</tr>
<tr>
<td><strong>Process Contingency - CO2 capture system</strong></td>
<td>N/A</td>
<td>5%</td>
<td>20%</td>
</tr>
<tr>
<td><strong>Project Contingency - Most plant components</strong></td>
<td>10.6%–26.5%</td>
<td>10.6%–26.5%</td>
<td>10.6%–26.5%</td>
</tr>
<tr>
<td><strong>Project Contingency - CO2 capture system</strong></td>
<td>16.7%</td>
<td>16.7%</td>
<td>40%</td>
</tr>
</tbody>
</table>

### 5.1.4.1 Fuel

Plant performance (in all three case studies) is based on the use of Illinois #6 coal as the fuel in the PC boiler. This coal type has an HHV of 27,135 KJ/kg (11,666 Btu/lb) as-received and is fed to the PC boiler (in all three cases) at a rate of 151,295 kg/h (333,542 lb/h). The overall thermal energy available from this coal is 1,140 MWh/hr. This value is used to calculate the net efficiency of each case study. This heating value conflicts with that stated in the DOE/NETL Systems Analysis Guidelines; however, the values from the EPRI report were used for consistency in comparison. Net efficiencies are listed in Table 20.

### 5.1.4.2 Capital Cost Year Dollars

All dollar values in Table 19 (and throughout this report) are provided in year 2005 U.S. dollars. To compare cost and performance values accurately across all three case studies, dollars reported in EPRI’s 2000 study were updated to 2005 dollars. To convert from year 2000 dollars into year 2005 dollars, indices from the Chemical Engineering Plant Cost Index (CEPCI) were used. CEPCI indices for the years 2000 and 2005 are 394 and 401.7, respectively.
5.1.4.3 Capacity Factor and Levelized Capital Charge Factor

EPRI’s 2000 report used a plant-operating capacity factor of 65%. To be consistent across all three case studies, a capacity factor of 65% was also used to evaluate the cost and power performance of a plant implementing the Dry Carbonate Process for CO₂ capture.

Similarly, EPRI’s report used a levelized capital charge factor of 14% for both Case 7A and Case 7C. The levelized capital charge is used to determine a levelized, over book life, bus bar cost of power and a cost per ton of CO₂ removed. Again, to be consistent, a levelized capital charge factor of 14% was used to evaluate the dry carbonate case.

5.1.4.4 Engineering Fees

Engineering fees represent the cost of architect/engineer services for engineering, design, drafting, and project management. A nominal 6% of the bare erected cost of each plant component was used for Cases 7A and 7C. In the dry carbonate study, an engineering fee of 6% was also assumed for both the dry carbonate unit itself and all other plant components.

5.1.4.5 Process and Project Contingency

Process contingency is applied to the overall cost of a certain technology and is designed to compensate for uncertainty in cost estimates caused by performance uncertainties of that particular technology. Process contingency is generally applied to systems (or equipment) that are not considered commercially mature. For Cases 7A and 7C, almost all of the systems and equipment are considered commercially mature, so no process contingency was assumed for these components. The exception was the CO₂ removal and compression system described in Case 7A, for which a 5.4% contingency was applied. According to DOE’s Carbon Capture and Sequestration Systems Analysis Guidelines, a 5.4% contingency is appropriate for a technology considered a “modification to a commercial technology.” Using this same reference, a process contingency of 20% was applied to the dry carbonate CO₂ capture system. A contingency value of 20% refers to a “new technology, with prototype test data.” This description fits the Dry Carbonate Process because it is a developing technology and because several aspects of the technology (e.g., sorbent performance, reaction rates, down-flow contacting) have been tested and verified. The other plant components in the dry carbonate case are considered commercially mature; therefore, no process contingency is applied.

Project contingency is also applied to the overall cost of different plant components, but this contingency is designed to compensate for cost uncertainties caused by incomplete technical definition. These contingencies are used to account for project escalation and the cost of any additional equipment.
that may result from a more detailed process design. Project contingencies for each plant component are
based on the level of detail and field experience with each component. Nominal contingency values of 5%
to 30% are used for the plant components of Cases 7A and 7C. In Case 7C, a contingency of 16.7% is
used for the CO2 removal system using MEA. This level of contingency is appropriate for a project that is
in the “project control” stages of development, according to the DOE’s systems analysis guidelines. The
Dry Carbonate Process is considered a “feasibility study,” and the associated project contingency for use
in the cost analysis is 40%. All other project contingencies for plant components in the dry carbonate case
are the same as those used in Case 7A and 7C studies.

5.1.5 Power Performance Comparison

Table 20 provides a detailed breakdown of the overall power performance of a power plant with
no CO2 capture, a power plant with CO2 capture using MEA, and a power plant with CO2 capture using
the Dry Carbonate Process. All values in the first two columns (Cases 7C and 7A) were taken from
similar tables presented in DOE’s systems analysis guidelines. The third column was added to compare
RTI’s Dry Carbonate Process to Cases 7C and 7A.

Overall, power performance is measured by Net Plant Power. Net Plant Power takes into account
the power produced by the steam turbine and generator, the generator losses (inefficiency), and the power
required by auxiliary equipment and systems.

As is seen in Table 20, the Net Plant Power shows a marked decrease from Case 7C to Case 7A.
Case 7A has a Net Plant Power of 329 MW, which represents a 28.8% decrease from the Net Plant
Power of Case 7C (462 MW). The Dry Carbonate Process represents only a 17.5% decrease, with a total
Net Plant Power of 381 MW.

5.1.5.1 Steam Cycle

The first section of Table 20 shows four variables associated with the steam cycle of the PC
boiler and steam turbine: throttle pressure, throttle temperature, reheat outlet temperature, and second
reheat outlet temperature. Because these variables are associated with the boiler and steam turbine, their
values remain unchanged regardless of the presence of a CO2 capture system in the overall plant design.
### Table 20. Power Performance for Case 7C, Case 7A, and Dry Carbonate Process Case

<table>
<thead>
<tr>
<th>Steam Cycle</th>
<th>w/o CO₂ Capture (Case 7C)</th>
<th>w/ CO₂ Capture (Case 7A)</th>
<th>w/ CO₂ Capture (Dry Carbonate)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Throttle Pressure, MPa (psig)</td>
<td>24.1 (3,500)</td>
<td>25.1 (3,500)</td>
<td>25.1 (3,500)</td>
</tr>
<tr>
<td>Throttle Temperature, °C (°F)</td>
<td>565.6 (1,050)</td>
<td>565.6 (1,050)</td>
<td>565.6 (1,050)</td>
</tr>
<tr>
<td>Reheat Outlet Temperature, °C (°F)</td>
<td>565.6 (1,050)</td>
<td>565.6 (1,050)</td>
<td>565.6 (1,050)</td>
</tr>
<tr>
<td>2nd Reheat Outlet Temperature, °C (°F)</td>
<td>565.6 (1,050)</td>
<td>565.6 (1,050)</td>
<td>565.6 (1,050)</td>
</tr>
<tr>
<td><strong>Consumables</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>As-Received Coal, kg/h (lb/h)</td>
<td>151,295 (333,542)</td>
<td>151,295 (333,542)</td>
<td>151,295 (333,542)</td>
</tr>
<tr>
<td>Sorbent, kg/h (lb/h)</td>
<td>15,535 (34,248)</td>
<td>15,535 (34,248)</td>
<td>15,535 (34,248)</td>
</tr>
<tr>
<td><strong>Gross Power Summary, kWe</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Steam Turbine Power</td>
<td>498,319</td>
<td>408,089</td>
<td>455,612</td>
</tr>
<tr>
<td>Generator Loss</td>
<td>(7,211)</td>
<td>(5,835)</td>
<td>(6,379)</td>
</tr>
<tr>
<td>Gross Plant Power</td>
<td>491,108</td>
<td>402,254</td>
<td>449,233</td>
</tr>
<tr>
<td><strong>Auxiliary Load Summary, kWe</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coal Handling and Conveying</td>
<td>390</td>
<td>390</td>
<td>390</td>
</tr>
<tr>
<td>Limestone Handling and Reagent Preparation</td>
<td>920</td>
<td>920</td>
<td>920</td>
</tr>
<tr>
<td>Pulverizers</td>
<td>1,860</td>
<td>1,860</td>
<td>1,860</td>
</tr>
<tr>
<td>Ash Handling</td>
<td>1,670</td>
<td>1,670</td>
<td>1,670</td>
</tr>
<tr>
<td>Primary Air Fans</td>
<td>1,220</td>
<td>1,220</td>
<td>1,220</td>
</tr>
<tr>
<td>Forced Draft Fans</td>
<td>970</td>
<td>970</td>
<td>970</td>
</tr>
<tr>
<td>Induced Draft Fans</td>
<td>5,050</td>
<td>19,880</td>
<td>13,663</td>
</tr>
<tr>
<td>SCR</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Seal Air Blowers</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Precipitators</td>
<td>1,000</td>
<td>1,000</td>
<td>1,000</td>
</tr>
<tr>
<td>FGD Pumps and Agitators</td>
<td>3,450</td>
<td>3,450</td>
<td>3,450</td>
</tr>
<tr>
<td>Condensate Pumps</td>
<td>590</td>
<td>300</td>
<td>590</td>
</tr>
<tr>
<td>Boilers Feed Water Booster Pumps</td>
<td>2,670</td>
<td>3,090</td>
<td>2,670</td>
</tr>
<tr>
<td>Miscellaneous (HVAC, lighting, control systems)</td>
<td>2,000</td>
<td>2,000</td>
<td>2,000</td>
</tr>
<tr>
<td>Steam Turbine Auxiliaries</td>
<td>400</td>
<td>400</td>
<td>400</td>
</tr>
<tr>
<td>Circulating Water Pumps</td>
<td>3,540</td>
<td>1,950</td>
<td>3,540</td>
</tr>
<tr>
<td>Cooling Tower Fans</td>
<td>2,030</td>
<td>1,110</td>
<td>2,030</td>
</tr>
</tbody>
</table>

(continues)
5.1.5.2 Steam Turbine Power

In all three power plant cases, the plant’s steam turbine consists of a very high pressure section, a high-pressure section, an intermediate-pressure section, and two double-flow low-pressure sections. All sections are connected to the generator by a common shaft. In the two CO₂ capture cases (Case 7A and the Dry Carbonate Process case), a significant amount of low-pressure steam is diverted from the plant’s steam cycle to use the steam’s inherent energy to regenerate the solvent (in Case 7A) or the solid sorbent (in the Dry Carbonate Process case). The diverting of this steam results in a net decrease in the achievable steam turbine power output. In Case 7A, 75 psia steam is taken away from the plant cycle for solvent regeneration; for comparison purposes, the dry carbonate case assumes the same steam conditions for regeneration of the sorbent material (it should be noted that this is a conservative estimate, because data suggests the Dry Carbonate regeneration can use steam at a lower pressure compared to MEA regeneration). The low-pressure steam enters the regenerator at 176.5°C [349.8°F] and provides 2204 kJ of thermal energy per kilogram of steam [947 BTU/lb], as taken directly from the mass and energy balances of the EPRI study. The EPRI report states that 1,216,000 lbs/hr of low pressure steam is withdrawn for MEA regeneration in Case 7A. This equals roughly 338 MW of thermal energy being diverted from power generation. Case 7A shows a decrease in steam turbine power of 90.2 MWe, therefore the EPRI report is claiming that 26.7% of the thermal energy withdrawn for solvent regeneration would have translated into electric power. Essentially, an efficiency of 26.7% is claimed. This same efficiency factor was used for the dry carbonate CO₂ capture case. Of the 2.95 million pounds per hour of
steam available in the power plant, the Dry Carbonate Process requires that 575,854 lbs/hr of steam (roughly 160 MW of thermal energy) be withdrawn at 75 psia for sorbent regeneration.

To determine the amount of steam required for sorbent regeneration, two heat values were calculated: the heat required to raise the sorbent temperature from 60° to 140°C (the sorbent-regeneration temperature) and the heat required to perform the decomposition reaction. The former heat value was calculated using the basic energy balance equation, taking into account the specific heats of NaHCO₃, Na₂CO₃, and alumina; the temperature rise of the sorbent; and the total amount of sorbent to be heated. The sorbent is assumed to be 67 wt% sodium carbonate on inert alumina reaching a sorbent CO₂ working capture capacity of 15 wt%. (Note: this CO₂ capture working capacity assumes that roughly 1 mol of Na₂CO₃ is available for every 0.5 mols of CO₂. Based on the data presented in this report – where the best working capacity is roughly a 0.1 to 1 molar ratio, this assumption is optimistic. It is, however, realistic based on new, 2nd generation sorbent materials being developed by RTI that exhibit working capacity ratios of roughly 0.6 to 1. The weight percentage of Na₂CO₃ on support quoted here is also based on new materials being developed and not data presented in this report – where 40 wt% Na₂CO₃ was the maximum loading. In addition to the above arguments, it is important to also note that these assumptions are reasonable given the desire to estimate the economics of a mature nth plant design). In this case, 208 MMBTU/hr of heat is required to bring the sorbent up to 140°C. The calculation used for the latter heat value (decomposition) is described below.

The heat of reaction for the bicarbonate decomposition reaction is 31.5 kcal/gmol CO₂. This value is multiplied by the total amount of CO₂ released by the sorbent to calculate the total heat required to perform the decomposition. The total heat required for the NaHCO₃ decomposition is 882 MMBTU/hr. This means a total of 1,090 MMBTU/hr of heat is required to fully regenerate the carbonate-based sorbent in RTI’s CO₂ capture system.

In general, most of this heat will be delivered by the steam taken from the plant’s steam cycle; however, not all of the heat has to come from steam because some can be delivered through heat integration. The Dry Carbonate Process has the potential for heat integration for two reasons: (1) heat is produced during the compression of the CO₂ product, (2) heat is available when the sorbent is cooled through indirect contact with cooling water, (3) heat is produced during the adsorption reaction and thus has potential for integration elsewhere in the process or the power plant as a whole. The heat produced in these two steps can be used to deliver heat required in the sorbent-regeneration process. At this point, it is very difficult to calculate the amount of heat integration that can be expected. Further testing is required to analyze these heat-integration techniques; however, to take into account the expected effect of heat
integration, it was assumed that one-half of the required regeneration energy is delivered by condensing steam, and the other half is delivered through heat integration. Therefore, roughly 546 MMBTU/hr of energy will come from the plant’s available steam. This value was used to determine the total amount of steam needed. (Note: again, it is important to note that these assumptions are reasonable given the desire to estimate the economics of a nth plant design of the Dry Carbonate Process).

For sorbent regeneration, low pressure steam at 75 psia and 176.5°C is condensed, and the heat of condensation is used to heat the sorbent. It was calculated that a total of 575 MMlbs/hr of 75 psia steam is required to fulfill the heat requirements of sorbent heating and sorbent regeneration. Using the same efficiency factor of 26.7%, removal of this steam from the power cycle reduces the steam turbine output by 77 MW. In total (including generator losses), the steam from the power plant steam cycle produces 449 MW of power, which is the amount of power that is expected from a power plant implementing the Dry Carbonate Process for CO₂ capture.

5.1.5.3 Generator Losses

Generator loss is a measure of the steam turbine generator’s efficiency. In both Case 7A and Case 7C, the steam turbine has an efficiency of nearly 98.6% (loss of 1.4%). In the dry carbonate case, the generator loss was calculated by assuming the same generator efficiency and multiplying 449 MW by 0.014. The generator loss in this case was 6.4 MW.

5.1.5.4 Gross Plant Power

Gross plant power refers to the amount of power actually produced by the plant (specifically, the steam turbine and generator) and is calculated by subtracting the generator loss from the steam turbine power. The Dry Carbonate Process case has a gross plant power of 449 MW, which represents a 11.7% increase in gross plant power output compared to Case 7A. The Dry Carbonate Process potentially represents an even greater improvement over the MEA case given the relatively early stages of development in comparison to the commercial deployment of the MEA process. A power plant implementing CO₂ capture with MEA has a gross plant power of 402 MW, which is an 18.1% decrease from the baseline; the Dry Carbonate Process shows a 8.6% decrease from the baseline. Further developments in process heat integration and sorbent capacity can significantly reduce the loss of gross plant power output.

5.1.5.5 Auxiliary Loads

Auxiliary load refers to the power required by auxiliary systems in a plant, thus decreasing the overall net power. Between Case 7C and Case 7A, the power required by 12 auxiliary systems remained
constant. It was assumed that these power requirements would also remain constant within a plant utilizing the Dry Carbonate Process because the 12 systems are mainly related to power production in the plant. The operation of these systems is unaffected by the insertion of a CO₂ removal system in the overall plant design. The 12 systems are (1) coal handling and conveying, (2) limestone handling and reagent preparation, (3) pulverizers, (4) ash handling, (5) primary air fans, (6) forced draft fans, (7) selective catalytic reducers, (8) sealed air blowers, (9) precipitators, (10) FGD pumps and agitators, (11) steam turbine auxiliaries, and (12) HVAC, lighting, and control systems.

Induced draft fans are required to move flue gas through control systems. One of the benefits of the entrained contactor configuration of the Dry Carbonate Process is that pressure drop is minimized. Instead of lifting the sorbent through a reactor (a configuration that would incur a significant pressure drop), the sorbent is entrained through the reactor co-currently with the flow of the flue gas. For this study, the induced draft fan power requirements for the dry carbonate system were calculated based on the power requirements already reported for Cases 7A and 7C. EPRI’s 2000 report suggests that Case 7C implements an induced draft fan after the plant’s electrostatic precipitator (ESP). These fans increase the gas pressure from 13.7 to 14.7 psia to move the flue gas through the rest of the plant. In Case 7A, the induced draft fans pressurize the flue gas from 13.7 to 17.7 psia to move the flue gas through the plant and, in particular, the MEA CO₂ capture system. The power requirements of the fans in these two cases are 5,050 kWe (1 psia, Case 7C) and 19,880 kWe (4 psia, Case 7A). Therefore, based on the average of these two cases, 5,010 kWe of power is required for every 1 psia of pressure. Using a formula for pressure drop in straight lengths of pipe, it was calculated that the dry carbonate system would incur an additional 0.018 psi of pressure drop above the baseline. Given the preliminary nature of this estimate and the fact that real systems may not be accurately predicted by these calculations, a safety factor was incorporated by multiplying the calculated pressure drop by 20. Therefore, the pressure drop through the dry carbonate system is 0.36 psi, and the dry carbonate plant case incurs an overall pressure drop of 1.36 psia. This value was multiplied by the average 5,010 kWe/pressure ratio to arrive at the overall requirement of the induced draft fans. Therefore, a power plant implementing the Dry Carbonate Process will require 6,814 kWₑ for the induced draft fans.

As for water and condensate pumping systems, it was assumed that the power requirements of Case 7C are the same as the requirements associated with the dry carbonate case. The reason for this is that both cases are closed-loop systems and require identical amounts of condensate and other water to be cooled and pumped through the plant. In Case 7C, steam is condensed to generate electricity using the steam turbine and generator. This condensate is then pumped back to the boiler for additional steam generation. It is assumed that no water is gained or lost in this process. In the dry carbonate case, some
steam is withdrawn from the plant’s steam cycle (unlike Case 7C), but this steam is used to indirectly heat and regenerate the carbonate-based sorbent in the CO₂-removal process. Upon heating the sorbent, the steam is condensed within the screw conveyors of the Dry Carbonate Process. This condensate can then be returned to the plant cycle and reused to generate steam; in essence, no water is gained or lost in this system. Therefore, it was assumed that all pumping and cooling requirements would be the same as for Case 7C because the same amount of water was being condensed and pumped. That is why Case 7C and the dry carbonate case have the same auxiliary load requirements for the condensate pumps, boiler feed water booster pumps, circulating water pumps, and cooling tower fans. Case 7A has lower power requirements (excluding for the booster pumps) because the steam withdrawn from the plant cycle is actually used in direct-contact heating of the MEA solution. Water is essentially lost in this cycle; therefore, smaller pumps (less power) are needed to circulate and cool the remaining water.

One of the largest auxiliary load requirements for both Case 7A and the dry carbonate case comes from the CO₂ removal and compression systems. The power required to operate these two CO₂ capture units are 1,940 kWe and 811 kWe, respectively. Because the Dry Carbonate Process is based on a straightforward, entrained-flow concept, little auxiliary load is required by this unit. The auxiliary load requirements come from the energy required to lift the sorbent with the system’s screw conveyors, and from cooling water pumps. This energy was determined by calculating the amount of potential energy change as the sorbent/water is lifted 30 vertical feet. An additional 15% was added to the auxiliary power demand of the water pumps to account for pressure losses. Any other auxiliary loads are assumed to be negligible.

The CO₂ compression system represents the single greatest auxiliary load requirement for both cases implementing CO₂ capture. EPRI’s 2000 report explains that the MEA capture system in Case 7A produces a nearly pure CO₂ stream, which is compressed to 1,222 psia by a multistage CO₂ compressor. This compression is done in preparation for sequestration of the CO₂ into geologic formations. Case 7A and the dry carbonate case both remove 90% of the CO₂ contained in coal-fired flue gas; therefore, the same amount of CO₂ will be compressed in both cases, and the auxiliary load required will also be identical. EPRI reported an auxiliary load of 29,730 kWe for the MEA system; this value was also used for the dry carbonate–equipped power plant. This pressure conflicts with that stated in the DOE/NETL systems analysis guidelines; however, the values from the EPRI report were used for consistency in comparison.
5.2 Operating Cost

Operating and maintenance costs are those costs associated with the day-to-day operation of the power plant and the CO₂ capture system, if applicable. Tables 21, 22, and 23 list the operating and maintenance costs for Case 7C, Case 7A, and the Dry Carbonate Process case, respectively.

5.2.1 Consumables

All chemicals, makeup sorbents, catalysts, fuel, etc., are considered consumables in the operation of a power plant. Tables 21, 22, and 23 list the estimated costs per year for each consumable. Also listed are the $/kW-yr and ¢/kWh values associated with these consumables. The ¢/kWh value was calculated assuming a 65% plant capacity factor. It was assumed that the amounts and costs of the consumables required in Case 7C were the same for the Dry Carbonate Process because the Dry Carbonate Process requires no additional chemicals, water, waste disposal, or fuel.

### Table 21. Operating and Maintenance Costs for Case 7C (dollars are in 2000 U.S. dollars except where indicated)

<table>
<thead>
<tr>
<th>Consumables</th>
<th>$ x 1,000</th>
<th>$/kW-yr 100% capacity</th>
<th>¢/kWh</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemicals (per ton/yr)</td>
<td>$6,304</td>
<td>$13.90</td>
<td>0.24469</td>
</tr>
<tr>
<td>Other Consumables (per ton/yr)</td>
<td>$2,966</td>
<td>$6.40</td>
<td>0.11215</td>
</tr>
<tr>
<td>Water (per 1,000 gal/yr)</td>
<td>$547</td>
<td>$1.20</td>
<td>0.02039</td>
</tr>
<tr>
<td>Mercury Removal (Activated Carbon, per ton/yr)</td>
<td>$0</td>
<td>$0.00</td>
<td>0</td>
</tr>
<tr>
<td>Waste Disposal (per ton/yr)</td>
<td>$3,380</td>
<td>$7.50</td>
<td>0.13254</td>
</tr>
<tr>
<td>By-Product Credits (per ton/yr)</td>
<td>$0</td>
<td>$0.00</td>
<td>0</td>
</tr>
<tr>
<td>Fuel Cost (per ton/yr)</td>
<td>$28,010</td>
<td>$60.40</td>
<td>1.06032</td>
</tr>
<tr>
<td>Operating &amp; Maintenance</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Operating Labor (per yr)</td>
<td>$4,909</td>
<td>$10.60</td>
<td>0.19</td>
</tr>
<tr>
<td>Maintenance Labor (per yr)</td>
<td>$2,686</td>
<td>$5.80</td>
<td>0.10</td>
</tr>
<tr>
<td>Administrative &amp; Support Labor (per yr)</td>
<td>$1,899</td>
<td>$4.10</td>
<td>0.07</td>
</tr>
<tr>
<td>Maintenance Material (per yr)</td>
<td>$4,030</td>
<td>$8.80</td>
<td>0.15</td>
</tr>
<tr>
<td>TOTALS (In year 2005 dollars)</td>
<td>$54,731</td>
<td>$118.70</td>
<td>2.08</td>
</tr>
</tbody>
</table>
Table 22. Operating and Maintenance Costs for Case 7A  
(dollars are in year 2000 U.S. dollars except where indicated)

<table>
<thead>
<tr>
<th>Item</th>
<th>$ x 1,000</th>
<th>$/kW-yr 100% capacity</th>
<th>¢/kWh</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Consumables</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chemicals (per ton/yr)</td>
<td>$10,447</td>
<td>$31.93</td>
<td>0.561</td>
</tr>
<tr>
<td>Other Consumables (per ton/yr)</td>
<td>$2,114</td>
<td>$6.39</td>
<td>0.112</td>
</tr>
<tr>
<td>Water (per 1,000 gal/yr)</td>
<td>$306</td>
<td>$1.16</td>
<td>0.02</td>
</tr>
<tr>
<td>Mercury Removal (Activated Carbon, per ton/yr)</td>
<td>$0</td>
<td>$0.00</td>
<td>0</td>
</tr>
<tr>
<td>Waste Disposal (per ton/yr)</td>
<td>$3,380</td>
<td>$10.45</td>
<td>0.184</td>
</tr>
<tr>
<td>Credits (per ton/yr)</td>
<td>$0</td>
<td>$0.00</td>
<td>0</td>
</tr>
<tr>
<td>Fuel Cost (per ton/yr)</td>
<td>$27,963</td>
<td>$85.35</td>
<td>1.499</td>
</tr>
<tr>
<td><strong>Operating &amp; Maintenance</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Operating Labor (per yr)</td>
<td>$5,375</td>
<td>$16.30</td>
<td>0.29</td>
</tr>
<tr>
<td>Maintenance Labor (per yr)</td>
<td>$3,558</td>
<td>$10.80</td>
<td>0.19</td>
</tr>
<tr>
<td>Administrative &amp; Support Labor (per yr)</td>
<td>$2,234</td>
<td>$6.60</td>
<td>0.12</td>
</tr>
<tr>
<td>Maintenance Material (per yr)</td>
<td>$5,337</td>
<td>$15.60</td>
<td>0.27</td>
</tr>
<tr>
<td>TOTALS (In year 2005 dollars)</td>
<td>$60,714</td>
<td>$185.00</td>
<td>3.24</td>
</tr>
</tbody>
</table>

Table 23. Operating and Maintenance Costs for Dry Carbonate Process Case  
(dollars are in year 2005 U.S. dollars)

<table>
<thead>
<tr>
<th>Item</th>
<th>$ x 1,000</th>
<th>$/kW-yr 100% capacity</th>
<th>¢/kWh</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Consumables</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chemicals (per ton/yr)</td>
<td>$6,304</td>
<td>$16.54</td>
<td>0.290</td>
</tr>
<tr>
<td>Other Consumables (per ton/yr)</td>
<td>$2,114</td>
<td>$5.54</td>
<td>0.097</td>
</tr>
<tr>
<td>Sorbent Make-up (per ton/yr)</td>
<td>$5,363</td>
<td>$21.64</td>
<td>0.247</td>
</tr>
<tr>
<td>Water (per 1,000 gal/yr)</td>
<td>$547</td>
<td>$1.44</td>
<td>0.025</td>
</tr>
<tr>
<td>Mercury Removal (Activated Carbon, per ton/yr)</td>
<td>$0</td>
<td>$0.00</td>
<td>0</td>
</tr>
<tr>
<td>Waste Disposal (per ton/yr)</td>
<td>$3,380</td>
<td>$8.87</td>
<td>0.156</td>
</tr>
<tr>
<td>By-Product Credits (per ton/yr)</td>
<td>$0</td>
<td>$0.00</td>
<td>0</td>
</tr>
<tr>
<td>Fuel Cost (per ton/yr)</td>
<td>$28010</td>
<td>$73.47</td>
<td>1.290</td>
</tr>
<tr>
<td><strong>Operating &amp; Maintenance</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Operating Labor (per yr)</td>
<td>$5,509</td>
<td>$14.45</td>
<td>0.254</td>
</tr>
<tr>
<td>Maintenance Labor (per yr)</td>
<td>$6,836</td>
<td>$17.93</td>
<td>0.315</td>
</tr>
<tr>
<td>Administrative &amp; Support Labor (per yr)</td>
<td>$1,941</td>
<td>$5.09</td>
<td>0.089</td>
</tr>
<tr>
<td>Maintenance Material (per yr)</td>
<td>$4,652</td>
<td>$12.20</td>
<td>0.214</td>
</tr>
<tr>
<td>TOTALS (In year 2005 dollars)</td>
<td>$64,656</td>
<td>$177</td>
<td>2.98</td>
</tr>
</tbody>
</table>
5.2.1.1 Sorbent Makeup

The Dry Carbonate Process uses a sorbent that requires periodic replacement. The carbonate-based sorbent used in the Dry Carbonate Process is a relatively robust material with a DI (attrition-resistance value) of 12. This material is stronger than most fluid catalytic cracking catalysts, which are the chemical industry’s standard for attrition resistance. Despite the sorbent’s superior physical strength, there is a certain amount of material loss expected from the mechanical transport associated with the screw conveyors of the Dry Carbonate Process. Based on the DI, it was estimated that 90 lbs of sorbent fines (<20 μm particles) per hour are produced for every 1,000,000 lbs of sorbent circulated in the system. Additionally, there is a loss of sorbent due to the irreversible reaction with SO₂. As described in the Executive Summary, only the loss due to reaction with SO₂ and other contaminants is counted in the sorbent replenishment rate. At a solids circulation rate of 16.5 MMlbs per hour, 418 lbs per hour of fines are generated. Sodium carbonate is tied-up at a rate of 471 lbs per hour due to the reaction with SO₂. The total sorbent replenishment rate thus matches the accumulation rate of SO₂ – 471 lbs per hour. The total sorbent makeup cost reflects the plant’s capacity factor of 65%. At a sorbent price of $2.00 per pound (as estimated by Süd-Chemie, Inc.) the annual sorbent replacement cost is $5,363,000 or .25 ¢/kWh, for the dry carbonate case.

5.2.1.2 Credits

Credits refer to the sale of any products not deemed as the main product of the power generation plant. In Cases 7A and 7C and the dry carbonate case, there are no other saleable products formed during the power-generation process.

5.2.2 Operating and Maintenance

Operating and maintenance costs take into account all of the plant labor (e.g., operational, maintenance, administrative, and support) and the materials needed to maintain the plant. Tables 21, 22, and 23 list the cost per year for plant labor and maintenance. Because Case 7C represents the baseline “no capture” plant, it can be assumed that the labor and maintenance costs associated with this plant can be carried over to the dry carbonate case. However, the labor and maintenance costs of operating the Dry Carbonate Process must be added to the baseline costs of Case 7C. This was the method used to evaluate the labor and maintenance costs of the dry carbonate case. To calculate these costs for the dry carbonate system itself, methods and formulas from Turton’s *Analysis, Synthesis, and Design of Chemical Processes* were used (Turton et al., 2003).
5.2.2.1 Operating Labor

According to Turton’s *Analysis, Synthesis, and Design of Chemical Processes*, the number of operators for a solids-handling process is determined by the following equation:

\[ N_{ol} = \left( 6.29 + 31.7 \times P^2 + 0.23 \times N_{np} \right)^{0.5} \]  

(8)

where

- \( P \) represents the number of solids handling steps,
- \( N_{np} \) is the total of process equipment parts, and
- \( N_{ol} \) is the number of operators required.

For the dry carbonate system, \( P \) equals two (adding fresh sorbent and removing fines) and \( N_{np} \) is equal to eight. Twelve operators are needed for the dry carbonate system, and a salary of $50,000 per year was assumed for each operator. Therefore, the total operating labor cost of this system is $600,000 per year. Added to the operating labor required in Case 7C, a plant utilizing dry carbonate CO\(_2\) capture will incur a total operating labor cost of roughly $5.5 million per year (It should be noted that it is unclear whether the EPRI report uses a similar method to calculate Case 7A operating labor. It is unclear whether these two calculated values can be compared directly).

5.2.2.2 Maintenance Labor

The maintenance labor cost is calculated as a function of the overall total capital requirement of the Dry Carbonate Process. According to Turton et al. (2003), maintenance costs represent 6% of the total capital requirement. Table 24 in Section 5.3 lists the total capital requirement of the Dry Carbonate Process as $69,161,730 (the method for calculating this value is described in Section 5.3.1.6). The cost of maintenance labor is $3.59 million. Added to the maintenance labor required in Case 7C, a plant using dry carbonate CO\(_2\) capture will incur a total maintenance labor cost of roughly $6.83 million per year (It should be noted that it is unclear whether the EPRI report uses a similar method to calculate Case 7A maintenance labor. It is unclear whether these two calculated values can be compared directly).

5.2.2.3 Administrative and Support Labor

The administrative and support labor cost is calculated as a function of the operating labor cost of the Dry Carbonate Process. According to Turton et al. (2003), administrative and support labor costs represent 18% of the operator’s salaries. The cost of this labor is $0.11 million. Added to the administrative and support labor required in Case 7C, a plant using dry carbonate CO\(_2\) capture will incur a total administrative and support labor cost of approximately $1.94 million per year.
5.2.2.4 Maintenance Material

The maintenance material cost is calculated as a function of the overall total capital requirement of the Dry Carbonate Process. According to Turton et al. (2003), maintenance costs represent 0.9% of the total capital requirement. The cost of maintenance material for the dry carbonate system is $0.62 million per year. Added to the maintenance material cost required in Case 7C, a plant using dry carbonate CO₂ capture will incur a total maintenance material cost of roughly $4.65 million per year.

5.2.3 Overall Operating and Maintenance Cost

The overall operating and maintenance costs of the plant incorporating dry carbonate CO₂ capture is calculated to be approximately $65 million. This represents a 18.1% increase over the plant with no CO₂ capture systems employed (Case 7C). The increase (in terms of overall cost) above the MEA system is 6.4%. However, these costs are based on the capital cost, which has been estimated rather conservatively and on assumptions that the methods of calculating operating and maintenance costs are the same as the EPRI report. As the research progresses, actual vendor and contractor quotes will be used to estimate the capital costs much more accurately than the theoretical models can predict, especially at such large scales.

5.3 Capital Cost

The capital costs for a power plant implementing CO₂ capture using the Dry Carbonate Process were estimated as shown in Table 24. Capital costs for Case 7C and Case 7A are also listed in Table 24 for comparison purposes.
Table 24. Process Capital and Total Capital Requirements for Case 7C, Case 7A, and Dry Carbonate Case (all amounts are in year 2005 U.S. dollars)

<table>
<thead>
<tr>
<th>Capital Cost Summary</th>
<th>No CO2 Capture (Case 7C) x $1,000 (2005 $)</th>
<th>With CO2 Capture (Case 7A) x $1,000 (2005 $)</th>
<th>With CO2 Capture (Dry Carbonate) x $1,000 (2005 $)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal and Sorbent Handling</td>
<td>$16,131</td>
<td>$16,131</td>
<td>$16,131</td>
</tr>
<tr>
<td>Coal and Sorbent Preparation and Feed</td>
<td>$12,652</td>
<td>$12,652</td>
<td>$12,652</td>
</tr>
<tr>
<td>Feedwater Systems</td>
<td>$25,340</td>
<td>$23,512</td>
<td>$25,340</td>
</tr>
<tr>
<td>PC Boiler and Accessories</td>
<td>$111,705</td>
<td>$111,083</td>
<td>$111,083</td>
</tr>
<tr>
<td>Flue Gas Cleanup</td>
<td>$62,688</td>
<td>$60,571</td>
<td>$60,571</td>
</tr>
<tr>
<td>Mercury Removal</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>CO2 Removal and Compression</td>
<td>NA</td>
<td>$113,953</td>
<td>$69,161</td>
</tr>
<tr>
<td>Combustion Turbine/Generator and Accessories</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>HRSG &amp; Stack</td>
<td>$20,945</td>
<td>$18,366</td>
<td>$18,366</td>
</tr>
<tr>
<td>Steam Turbine Generator and Accessories</td>
<td>$74,309</td>
<td>$63,461</td>
<td>$69,126</td>
</tr>
<tr>
<td>Cooling Water System</td>
<td>$19,967</td>
<td>$17,468</td>
<td>$19,967</td>
</tr>
<tr>
<td>Ash/Sspent Sorbent Handling System</td>
<td>$19,628</td>
<td>$19,628</td>
<td>$19,628</td>
</tr>
<tr>
<td>Accessory Electric Plant</td>
<td>$24,624</td>
<td>$31,954</td>
<td>$31,122</td>
</tr>
<tr>
<td>Instrumentation &amp; Controls</td>
<td>$9,524</td>
<td>$9,053</td>
<td>$9,053</td>
</tr>
<tr>
<td>Buildings &amp; Structures</td>
<td>$36,397</td>
<td>$34,354</td>
<td>$34,354</td>
</tr>
<tr>
<td>Process Capital</td>
<td>$433,909</td>
<td>$532,185</td>
<td>$496,554</td>
</tr>
<tr>
<td>Engineering Fees</td>
<td>$26,035</td>
<td>$31,931</td>
<td>$29,793</td>
</tr>
<tr>
<td>Process Contingency</td>
<td>NA</td>
<td>$6,142</td>
<td>$8,232</td>
</tr>
<tr>
<td>Project Contingency</td>
<td>$66,572</td>
<td>$83,046</td>
<td>$84,986</td>
</tr>
<tr>
<td>Allowable Funds Used During Construction</td>
<td>$43,679</td>
<td>$53,963</td>
<td>$49,655</td>
</tr>
<tr>
<td>Land Cost</td>
<td>$522</td>
<td>$555</td>
<td>$531</td>
</tr>
<tr>
<td>Inventory Capital</td>
<td>$5,638</td>
<td>$6,439</td>
<td>$8,466</td>
</tr>
<tr>
<td>Preproduction Costs</td>
<td>$15,358</td>
<td>$18,738</td>
<td>$17,379</td>
</tr>
<tr>
<td>Total Capital Requirement (TCR)</td>
<td>$591,714</td>
<td>$733,000</td>
<td>$695,598</td>
</tr>
</tbody>
</table>

HSRG = Heat Recovery Steam Generator

5.3.1 Process Capital

The process capital requirements for a power plant implementing the Dry Carbonate Process for CO2 capture were estimated as shown in Table 24. A full cost analysis of an entire Dry Carbonate Process–equipped power plant was not conducted; many of the process capital requirements for equipment used in the dry carbonate case were either assumed or interpolated based on information.
provided for the two “baseline” cases (Case 7C and Case 7A). It is assumed that many plant components/systems will be similar if not identical across all three cases.

5.3.1.1 Coal and Sorbent Handling, Preparation, and Feed

The coal handling, preparation, and feed systems provide the equipment for the proper delivery and preparation of the coal that is fed to the plant’s boiler. These systems do not change with the addition of a carbon-capture unit downstream of the boiler; thus, the capital equipment cost of these systems is consistent across all three cases.

5.3.1.2 Ash and Spent Sorbent Handling System

The ash and spent sorbent handling system provides the equipment for the proper removal and storage of the fly ash and bottom ash produced daily by the boiler, as well as the proper handling of the spent sorbent from the WFGD system. These systems do not change with the addition of a carbon capture unit; thus, the capital equipment cost of these systems is consistent across all three cases.

5.3.1.3 Feedwater and Cooling Water Systems

For reasons described in Section 5.1.5.5, the feedwater and cooling water systems in the dry carbonate plant case are assumed to be nearly identical to these same systems in Case 7C (no capture). Therefore, the capital costs of these systems for the “no capture” case were also used in the dry carbonate case.

5.3.1.4 PC Boiler and Accessories

The PC boiler and accessories should be nearly identical across all three plant cases in terms of size, design, operating conditions, and cost. Table 24 shows that the reported capital costs of these components are nearly identical. Because Case 7A relates more closely to the dry carbonate case (both employ CO₂ capture systems), it was assumed that the PC boiler and accessories of the dry carbonate case would have the same capital cost as Case 7A.

5.3.1.5 Flue Gas Cleanup

The FGD system employed in all three plant cases is a wet, limestone-based system that is designed to remove 98% of the SO₂ in the flue gas before the gas is released through the stack. The flue gas cleanup system should be nearly identical across all three plant cases in terms of size, design, operating conditions, and cost. Table 24 shows that the reported capital costs of these components are very similar. Because Case 7A relates more closely to the dry carbonate case (both employ CO₂ capture
systems), it was assumed that the flue gas cleanup of the dry carbonate case would have the same capital cost as Case 7A.

5.3.1.6 Carbon Dioxide Removal and Compression

The basis of the dry carbonate system capital cost estimates was a flue gas rate of 130,000 SCFH per MWₑ capacity (consistent with the EPRI report) and a desulfurized flue gas concentration of 11.5 vol% CO₂ at the outlet of WFGD. The CO₂ capture process for a 500 MWₑ (nominal) power plant would be required to treat about 54 million SCFH of flue gas and collect about 3 million tons of CO₂ annually (90% removal, 100% capacity factor assumed). Dividing this flow into two parallel entrained flow adsorbers of 30 feet in diameter and 325 feet in length meets the adsorber residence time requirement for the sorbent. A 25-second residence time was assumed in the adsorber sizing. The scope of this capital cost estimate includes the following:

- Two downflow contactors
- One solids bin
- Three pumps (two for cooling water, one for regeneration off-gas condensate)
- Regenerator off-gas condenser
- Four screw conveyors (regeneration and cooling screw conveyors, two each)
- Four screw motors (for each screw conveyor)
- One CO₂ compressor

No backup equipment was assumed for the capital cost estimates, which is consistent with the EPRI approach for the MEA CO₂ capture system (EPRI, 2000).

All capital cost estimates (excluding those for the CO₂ compressor) were made using Turton’s *Analysis, Synthesis, and Design of Chemical Processes* (Turton et al., 2003). The equation used to calculate the estimated purchase cost of each piece of equipment was as follows:

$$\log_{10} C_p^r = K_1 + K_2 \log_{10} (A) + K_3 [\log_{10} (A)]^2$$  \hspace{1cm} (9)

where

- $C_p$ is the purchased cost;
- $K_1$, $K_2$, and $K_3$ are the purchase price constants (listed in Appendix A of Turton et al., 2003); and
- $A$ represents the sizing value.
The sizing value $A$ was calculated for each piece of equipment based on the unit of measure required to size the equipment. This equation was used to estimate the capital costs of all equipment listed above, except the CO$_2$ compressor.

It should be noted that because of the size of the equipment required for the dry carbonate CO$_2$ capture system, the equipment sizes exceeded the size limitations of the model described above. For each case in which the equipment size exceeded limitations, the maximum size was used in the model’s calculations, and a linear multiplier was then used based on the extent to which the size exceeded the maximum, based on the model. For instance, the cooling water pump was sized to 576 kW; the model had a maximum size of 300 kW. The 300 kW size was used in the model and that value was then multiplied by 576/300, or 1.92, to determine the capital cost for the pump.

The ideal method of calculating the CO$_2$ compressor cost for the dry carbonate case would be to assume the same cost as for the compressor in Case 7A, because the quantity of CO$_2$ being compressed in each of these cases is identical. EPRI’s report (EPRI, 2000) does not list the compressor costs separately; therefore, the same value cannot be used. Alstom Power, Inc., produced a CO$_2$ capture study that identified the CO$_2$ compressor costs to be 16.2% of the total capital cost of an MEA system similar to the one described in Case 7A (Alstom Power, 2001). RTI received feedback from DOE-NETL that their Integrated Environmental Control Model (IECM) has estimated a compressor cost of roughly $28 million for a case similar to Case 7A. Drying costs were also estimated by IECM, but these costs are accounted for by RTI’s own calculations for condenser and pump costs. RTI decided to use the IECM compressor value as a ballpark cost for the Dry Carbonate compressor. $28 million was added to the total cost of all other dry carbonate system equipment (~ $41 million), bringing the estimated total capital cost of the dry carbonate system to $69.1 million. As for contingency values for the CO$_2$ compressor, a process contingency of 0% and a project contingency of 10.6% were assumed, because the compressor is a well-known, commercially mature piece of equipment. A 0% process contingency is consistent with DOE’s systems analysis guidelines for a “commercial technology.” A 10.6% project contingency was assumed, because this is the value used for the flue gas clean-up system, which also comprises commercially available equipment.

### 5.3.1.7 Heat Recovery Steam Generator and Stack

An HRSG system and an exhaust stack are employed in all three cases. The stack in each case is constructed of reinforced concrete and is provided with a single, fiberglass-reinforced plastic liner. The HRSG and stack should be very similar across all three plant cases in terms of size, design, operating conditions, and cost. Table 24 shows that the reported capital costs of these components are nearly
identical for Cases 7A and 7C. Because Case 7A relates more closely to the dry carbonate case (both employ CO₂ capture systems), it was assumed that the HRSG and stack of the dry carbonate case would have the same capital cost as for Case 7A.

5.3.1.8 Steam Turbine Generator and Accessories

The steam generator used in the plant incorporating the Dry Carbonate Process for CO₂ capture is described in Section 5.1.5.2. The steam generators used in Cases 7A and 7C are similar to that used in the dry carbonate case, differing only in size and the types and number of accessories used. It was assumed that the capital cost of the steam turbine generator and accessories is a function of the steam turbine power produced (i.e., size of generator and accessories used). Because the amount of power produced in the dry carbonate case falls between the power values shown in Cases 7A and 7C, it was assumed that the cost of the generator and accessories should also fall between the costs of these components in the two EPRI cases. The steam generator cost in the dry carbonate case was calculated based on a linear function of the cost versus power produced for Cases 7A and 7C (with these cases representing the two end points of the line). Using this method, the steam generator and accessories have an estimated capital cost of roughly $69.1 million.

5.3.1.9 Accessory Electric Plant

The accessory electric plant is used to power all auxiliary equipment and systems in the three power plant cases. The accessory electric plant consists of all switchgear and control equipment, generator equipment, station service equipment, conduit and cable trays, and all wire and cable. It also includes the main power transformer, required foundations, and standby equipment. It was assumed that the capital cost of the accessory electric plant is a function of the auxiliary load requirements. Because the auxiliary loads in the dry carbonate case fall between those shown in Case 7A and Case 7C, it was assumed that the cost of the electric plant should also fall between the costs indicated in these two cases. The electric plant cost in the dry carbonate case was calculated based on a linear function of the cost versus load requirements of Cases 7A and 7C (with these cases representing the two end points of the line). Using this method, the capital cost of the accessory electric plant was estimated at nearly $31.1 million.

5.3.1.10 Instrumentation and Controls

The instrumentation and controls system consists of an integrated plant-wide control and monitoring system with a control room housing multiple computers that act as the interface between the generating process and the operations personnel. This system is employed in all three plant cases and
should be nearly identical in terms of size, design, and cost. Table 24 shows that the reported capital costs of these components are very similar for Cases 7A and 7C. Because Case 7A relates more closely to the dry carbonate case (both employ CO₂ capture systems), it was assumed that the instrumentation and controls system for the dry carbonate case would have the same capital cost as for Case 7A.

5.3.1.11 Buildings and Structures

EPRI provides a list of the buildings and structures required for Cases 7A and 7C. The buildings and structures required for the Dry Carbonate Process should be nearly identical to those required for Case 7A and Case 7C. Table 24 shows that the reported capital costs of these components for Cases 7A and 7C are very similar. Because Case 7A relates more closely to the dry carbonate case (both employ CO₂ capture systems), it was assumed that the buildings and structures required in the dry carbonate case would have the same capital cost as for Case 7A.

5.3.2 Other Capital Requirements

To estimate the total capital requirement for a power plant, the fees, contingencies, and other capital needs must be included, in addition to the capital cost of systems and equipment. The engineering fees, process contingency, and project contingency listed in Table 19 are described in Section 5.1.4 of this report. Descriptions of the remaining capital requirements follow.

5.3.2.1 Allowable Funds Used During Construction

Although this topic is not clearly discussed in EPRI’s report, it was assumed that the allowable funds used during construction refer to the funds required to provide temporary services and facilities onsite while the plant is being built. Cases 7A and 7C indicate that allowable funds are calculated by assuming 10% of the estimated capital cost of the plant. For the dry carbonate case, the allowable funds used during construction were estimated at approximately $49.7 million.

5.3.2.2 Land Cost

The cost of land (per acre) is provided in EPRI’s report and is assumed to be consistent across all three plant cases. EPRI reports that the cost of land is $1,631 per acre in the East-West region (this is also listed in Table 19 of Section 5.1.4). EPRI estimates that a plant built with no CO₂ capture facility (Case 7C) incurs a land cost of $522,000; therefore, the plant occupies approximately 320 acres. The plant that implements CO₂ capture using an MEA system has a land cost of $554,600 and so occupies approximately 340 acres, meaning the MEA system adds a total of 20 acres to the overall land requirement of the plant. However, a 2001 Alstom Power report estimates that an MEA system requires
only seven additional acres (Alstom Power, 2001), whereas EPRI’s requirement is three times this value. It was estimated that the Dry Carbonate Process will require an addition of approximately two acres to the overall area of a plant. To be more conservative in this estimate (and more consistent with EPRI’s report), it was assumed that the actual land requirement would be three times this value (six acres); the cost of land in the dry carbonate case was thus calculated at $0.53 million.

5.3.2.3 Inventory Capital

Inventory capital refers to the funds required to begin power production with a 30-day inventory of fuels, chemicals, and other consumables. It was assumed that the dry carbonate inventory includes the inventory required for the actual power plant (Case 7C) plus the sorbent inventory required for the Dry Carbonate Process. This sorbent inventory includes both the initial loading for the system and the makeup sorbent required for the first 30 days of operation. The initial sorbent loading was calculated based on the assumed residence time of the sorbent in the Dry Carbonate Process (10 min) and the circulation rate of the sorbent (about 2,322 tons per hour). The sorbent required for the initial loading is about 388 tons and costs roughly $1.6 million. The sorbent makeup rate is described in Section 5.2.1. In a 30-day period (assuming a 100% capacity factor), the replacement sorbent requirement is about 170 tons and costs $1.3 million; therefore, the overall inventory capital required for the dry carbonate case is roughly $8.47 million (this includes the inventory capital required in Case 7C).

5.3.2.4 Preproduction Costs

Although preproduction costs are not clearly discussed in EPRI’s report, it was assumed that these costs refer to the funds required to start the project before construction can begin (e.g., permitting costs, submitting proper documentation, and planning). Cases 7A and 7C indicate clearly that the preproduction costs are calculated by assuming 3.5% of the estimated capital cost of the plant. For the dry carbonate case, the preproduction cost was estimated at approximately $17.4 million.

5.3.3 Total Capital Requirement

The TCR of a power plant incorporating the Dry Carbonate Process for CO₂ removal is roughly $696 million. This represents a 20.0% increase over the no-capture case and a 5.0% savings over the plant with amine-based scrubbing for CO₂ removal.

5.4 Overall Economic Performance

Overall economic performance is the true measure of how the dry carbonate case compares to Cases 7A and 7C. Table 25 lists the measures of economic performance that DOE regards as most
important when comparing experimental systems to other, more established systems (as described in the DOE NETL’s Carbon Capture and Sequestration Systems Analysis Guidelines). DOE is most interested in the overall COE (on $/kWh basis, after accounting for the levelized charge factor) and the cost of capturing CO₂ (on a $/ton of CO₂ removed basis). Levelized capital charge factor and capacity factor are explained in Section 5.1 of this report. Overall, COE is calculated by adding together the capital cost (on a $/kWh basis) and the production costs (on a $/kWh basis) of the power plant. The capital cost is listed in Table 25, and the production costs of the three cases are found in Tables 21, 22, and 23. The baseline plant (Case 7C) removes zero tons of CO₂; therefore, this case has no associated CO₂ removal costs. It can be assumed that the increased cost of Case 7A and the dry carbonate case (compared to Case 7C) is solely due to implementing CO₂ capture. The difference in overall COE was used to calculate the cost of CO₂ removed. Also, it is a widely used assumption (confirmed by EPRI Case 7C) that for every 1 kWₑ of power generated, 1 kilogram (2.205 lbs) of CO₂ is produced. To arrive at a “$/ton of CO₂ removed” value, the difference in COE ($/kWh) for the two capture cases was first divided by 100 to convert cents into dollars and then divided by 2.205 lbs of CO₂ to arrive at a $/lbs CO₂ value. The result was then multiplied by 2,000 lbs to get a $/ton of CO₂ removed value.

### Table 25. Overall Cost of Electricity and Dollars per ton of Carbon Dioxide Removed for Case 7C, Case 7A, and Dry Carbonate Process Case (all amounts are in year 2005 U.S. dollars)

<table>
<thead>
<tr>
<th>Capital Cost Summary</th>
<th>No CO₂ Capture (Case 7C)</th>
<th>With CO₂ Capture (Case 7A)</th>
<th>With CO₂ Capture (Dry Carbonate)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Levelized Capital Charge Factor (%)</td>
<td>14%</td>
<td>14%</td>
<td>14%</td>
</tr>
<tr>
<td>Capacity Factor (%)</td>
<td>65%</td>
<td>65%</td>
<td>65%</td>
</tr>
<tr>
<td>CO₂ Capture Rate (%)</td>
<td>N/A</td>
<td>90%</td>
<td>90%</td>
</tr>
<tr>
<td>Gross Plant Power (MWₑ)</td>
<td>491.1</td>
<td>402.3</td>
<td>449.2</td>
</tr>
<tr>
<td>Net Plant Power (MWₑ)</td>
<td>462.1</td>
<td>329.3</td>
<td>381.2</td>
</tr>
<tr>
<td>Capital c/kWh</td>
<td>3.43</td>
<td>5.47</td>
<td>4.49</td>
</tr>
<tr>
<td>Production c/kWh</td>
<td>2.08</td>
<td>3.24</td>
<td>2.98</td>
</tr>
<tr>
<td>Total c/kWh</td>
<td>5.51</td>
<td>8.73</td>
<td>7.46</td>
</tr>
<tr>
<td>Increase in COE (%)</td>
<td>N/A</td>
<td>58.4%</td>
<td>35.4%</td>
</tr>
<tr>
<td>$/ton CO₂ Removed</td>
<td>N/A</td>
<td>29.19</td>
<td>17.72</td>
</tr>
</tbody>
</table>

Overall, the economic performance of the plant incorporating dry carbonate CO₂ capture is quite good when compared to that of Case 7C. The COE increase of the dry carbonate case is 1.95 cents per kWh, or 35.4% increase over the no-capture case. This estimated cost increase is slightly higher than DOE targets of limiting COE increase to 35%, but the Dry Carbonate Process is well below the cost of electricity value associate with MEA (58.4% increase) and roughly 16% more energy efficient than conventional MEA technology – based on Net Plant Power figures (DOE cost targets for CO₂ capture technologies are provided in the DOE National Energy Technology Laboratory’s (DOE/NETL’s) Carbon
Further research and development should bring that value below the 35% COE increase goal parameters. The cost of CO₂ removal is 17.72 $/tons of CO₂ removed for the dry carbonate case. In comparison to Case 7A, this is an 39% savings over the MEA system.

6.0 Conclusions

An optimized Na₂CO₃-based sorbent prepared at a commercial manufacturing facility maintained its reactivity over several hundred adsorption and regeneration cycles as well as after exposure to natural gas– and coal-derived flue gases in a pilot-scale, entrained-bed reactor system. After 14 months of entrained-bed testing and an estimated several thousand cycles through the bench scale screw conveyor system, no significant attrition of the sorbent was observed. This sorbent is capable of removing >90% of the CO₂ in flue gas for an expected entrained-bed reactor adsorption residence time of 20 to 30 seconds.

Laboratory studies indicate that 15 wt% of supported Na₂CO₃ sorbent will absorb significant quantities of CO₂ from simulated flue gas in a downflow co-current reactor system with a gas-solids contact time of approximately 15 seconds. The reaction occurs at temperatures between 25°C and 62°C and is favored by low temperatures and high sorbent-to-gas ratios. Maximum CO₂ removals of >90% were achieved from a simulated flue gas containing 15% CO₂ at gas residence times of 60 to 80 seconds at 20°C. Additionally, >90% CO₂ capture was observed using fossil fuel–derived flue gas at 60°C, with residence times as short as 30 seconds.

Na₂CO₃-based sorbents react rapidly and (under expected regeneration conditions) irreversibly with SO₂ and HCl, which are expected trace contaminants in desulfurized flue gas from coal-fired power plants. The sorbent adsorbed little or no Hg vapor from a gas mixture containing 460 µg/dscm (cubic meter of dry standard) of elemental mercury in He. After 104 hours of exposure to coal-derived flue gas, no appreciable difference in sulphate or chloride ions on the sorbent was observed.

CO₂ removal from power plant flue gas using the dry carbonate sorbent process is less energy intensive and less expensive than removal using an MEA liquid absorption system. A comparative economic analysis of the processes, as applied to a baseline 500 MWₑ (nominal) plant without CO₂ removal, suggests that implementation of the Dry Carbonate Process would result in an increase in the COE of 1.95 cents/kWhr, in contrast to an increase of 3.2 cents/kWhr for an MEA system. The 1.95 cents/kWhr represents an increase in the COE of about 35.4%. Assuming a 65% capacity factor for the plant and a levelized capital charge of 14% of the incremental capital cost, the estimated CO₂ removal
cost for the dry carbonate system is about $17.7/ton CO₂. These cost and power performance values were calculated using realistic data generated in laboratory testing. It is anticipated that further development of the RTI Dry Carbonate Process will only increase its economic advantage over MEA systems and that the main areas of improvement for this process will be in higher percentages of heat integration from process heats, higher sorbent loading capacity, much lower pressure drop across the system, and lower value (lower pressure) steam being used for regeneration.

7.0 Recommendations for Future Work

RTI has demonstrated that the Dry Carbonate Process for CO₂ capture is capable of >90% removal of CO₂ from actual coal-fired and natural gas-fired flue gas. We have further demonstrated that this technology has the potential to be significantly cheaper than conventional amine-based CO₂ capture technologies. Despite these two important accomplishments, there is still plenty of development required to reach a commercial embodiment of this process. The two main areas for additional development are process development and sorbent development. The following recommendations are made for further development of this process to make it a commercial reality:

- Evaluate new process designs that incorporate heat removal techniques to control temperature rise in the adsorber. This involves evaluating the technical and economic feasibility of multiple process configurations.

- Evaluate new process designs for the sorbent regenerator that focus on transferring heat in the most efficient way possible. This involves evaluating the technical and economic feasibility of multiple process configurations.

- Conduct heat integration studies to evaluate the feasibility of using process heats and available heat in a power plant to reduce the energy penalty associated with sorbent regeneration.

- Conduct a study to evaluate process integration within a power plant.

- Conduct bench-scale parametric studies of the most promising process designs for proof-of-concept testing before scale-up to a larger research unit.

- Following proof-of-concept testing, build a larger research unit capable of removing significant amounts of CO₂ from actual fossil fuel-fired flue gas. Operate this system for thousands of hours to test long-term performance and reliability of the Dry Carbonate process.

- Conduct a significant update of the economic analysis based on a new process design.

- Evaluate sorbent manufacturing technique and determine whether it needs to be modified for a new process design. Develop ways to drive down cost of sorbent manufacture.
8.0 References


