The "Dry Carbonate" Sorbent Technology for CO_2 Removal from Flue Gas of Existing Coal-fired Power Plants

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ABSTRACT

The reversible reaction between sodium carbonate, CO_2 and H_2O, to form sodium bicarbonate can be used in a thermal-swing process to recover concentrated CO_2 from power plant flue gas. A process based on this reaction has been developed.

Field testing of a prototype "Dry Carbonate Process" has been conducted using natural gas-derived and coal-derived flue gases from a combustor. Greater than 90% removal of CO_2 was achieved during testing. The system was exposed to flue gas for over 230 hours and the most promising process conditions were determined from collected data. Pollutants in the flue gas had no effect on sorbent performance. The sorbent showed little physical attrition over hundreds of cycles. An economic evaluation shows the "Dry Carbonate Process" has significant advantages over existing technologies. Modifications to the process have been considered and additional research will be conducted before constructing a pilot-scale unit capable of capturing 1 ton/day CO_2.

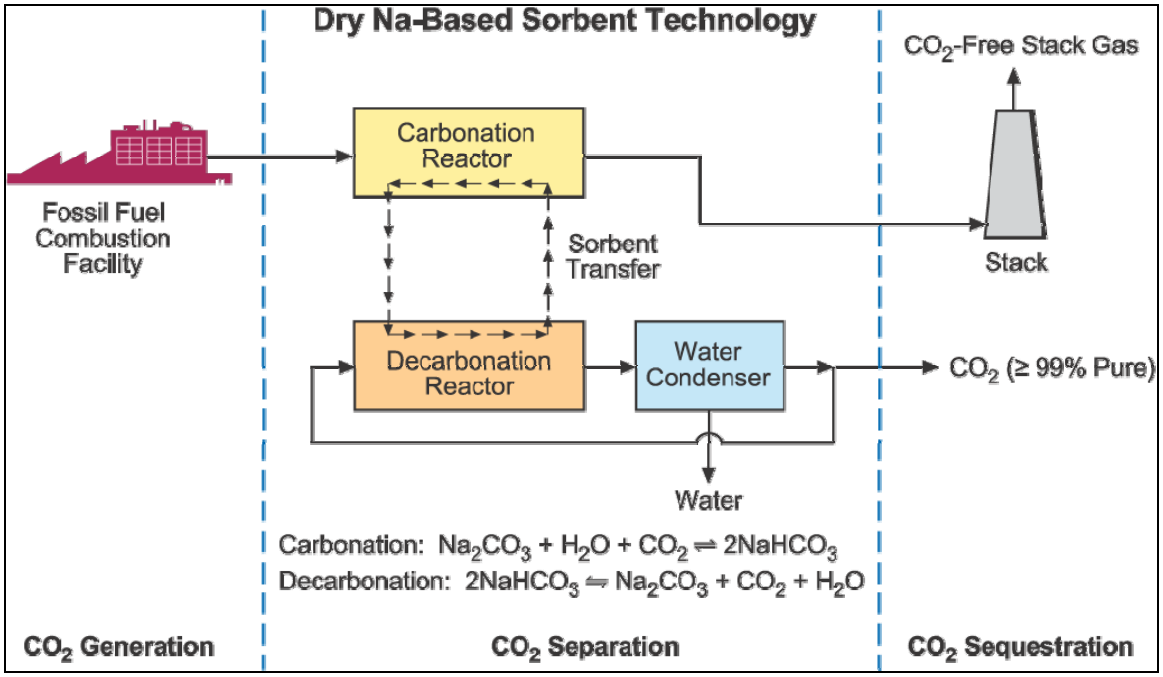
INTRODUCTION

Mitigation of carbon dioxide (CO_2) emissions from coal-fired power plants is a growing area of interest for the utility industry. Although there are no current environmental regulations for CO_2 emissions, the utility industry is actively exploring options for capture and sequestration of CO_2. These options include more efficient power cycles, oxy-combustion, and CO_2 scrubbing technologies, such as liquid solvents, primarily based on amines and monoethanolamine (MEA). Existing amine-based systems can be commercially utilized; however, they have a number of major disadvantages, including high parasitic steam loss due to solvent regeneration, sensitivity to SO_X and O_2, solvent loss due to vaporization, and high capital and operating costs.

In a research and development project funded by the U.S. Department of Energy's National Energy Technology Laboratory (DOE/NETL), RTI International (RTI) has been developing a process to capture CO_2 from power plant flue gas using an inexpensive, dry, regenerable adsorbent (sorbent). The overall focus of this project is to develop a technology that has significant cost and energy efficiency advantages compared to existing amine-based CO_2 capture processes.

RTI's CO_2 capture process – the Dry Carbonate Process – makes use of the well-known reaction chemistry of sodium carbonate (Na_2CO_3 or soda ash) and sodium bicarbonate ($NaHCO_3$ or baking soda). Sodium carbonate captures CO_2 in the presence of water (H_2O) to form sodium bicarbonate. Increasing the process temperature causes the bicarbonate to decompose and release a CO_2/steam mixture that can be converted into a pure "sequestration-ready" CO_2 gas stream. This process is intended as a retrofit to existing plants and is ideally suited for coal-fired power plants incorporating wet flue gas desulfurization (WFGD) – due to the associated cooling and saturation of the flue gas. A basic schematic of the Dry Carbonate Process is shown in Figure 1.

Figure 1: Basic Schematic of RTI's Dry Carbonate Process



Process development (based on a novel process design) has been successfully completed at bench-scale. This bench-scale system is being used to demonstrate the technology by treating actual flue gas from a small-scale boiler (1 MWt). Throughout the project, RTI's sorbent has consistently demonstrated greater than 90% CO_2 removal from simulated flue gas over multiple cycles of absorption and regeneration (CO_2 capture and CO_2 release). Preliminary economic analysis indicates that a power generation facility would incur an approximate 20% increase in the cost of electricity by implementing RTI's CO_2 removal technology in a 500MW coal-fired power plant.

PROJECT HISTORY

Capture of CO_2 using sodium carbonate results in the reversible formation of sodium bicarbonate ($NaHCO_3$):

$$Na_2CO_3(s) + CO_2(g) + H_2O(g) \leftrightarrow 2NaHCO_3(s) \qquad \Delta H_r^o = -1325 \text{ Btu/lb } CO_2 \qquad (1)$$

This reaction (CO_2 absorptions) is highly exothermic. The equivalent reverse reaction (sorbent regeneration) is endothermic and produces an equal molar quantity of CO_2 and H_2O. Condensation of H_2O from the regeneration product results in a pure CO_2 stream suitable for sequestration or reuse.

Initial research on this project was conducted using thermogravimetric analysis (TGA) in order to gain a full understanding of the chemistry involved as well as to prove the feasibility of the carbonate-based sorbent to remove CO_2 under realistic flue gas conditions. Sorbent precursors used in the preliminary research included various grades of sodium bicarbonate and trona (a naturally occurring sodium-based mineral).

Based on observations from TGA studies, RTI designed and carried out several fixed-bed and fluidized-bed tests with simulated flue gas to evaluate sorbent performance in adsorption and regeneration "modes". The goal of this effort was to measure the extent of removal capacity of the carbonate sorbents as well as evaluate their performance over several cycles. Highlights of these studies include:

- CO_2 removal of greater than 90% is possible
- No deactivation was observed over multiple cycles
- Rapid initial CO_2 removal rates were observed in fluidized-bed tests
- Temperature rise during adsorption caused decline in removal rates

Due to the observed sorbent temperature rise, it was clear that fixed-bed and dense-phase fluidized-bed systems are not optimal reactor schemes for the Dry Carbonate Process. Continuous CO_2 removal of 90% cannot be accomplished in these reactor environments, because the poor heat transfer and poor heat removal inherent to these systems causes 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 effectively as well as carry out adsorption and regeneration continuously. To this end, RTI considered using an entrained-bed type system for the design of the Dry Carbonate Process.

Supported Sorbents

RTI's sorbent development activities have progressively narrowed the scope of which sorbents and process designs can combine to work as a commercially feasible CO_2 capture process. Raw forms of sodium carbonate (soda ash, trona, calcined bicarbonate) were tested first due to their attractiveness as abundant and cheap materials. However, supported sorbents (Na_2CO_3 on an inert support material) and various methods of preparation were explored in order to capitalize on the higher surface area and physical strength associated with these materials. RTI has 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. The most promising sorbents were subjected to fluidized-bed testing in simulated flue gas to get a realistic measure of sorbent performance. These efforts have to the development of a sorbent which is suitable for use in a commercial entrained-bed reactor. In order to prove this (and to obtain data on sorbent life and CO_2 reactivity), RTI tested the supported sorbent in a bench-scale entrained-bed unit at the CANMET Energy Technology Centre in Ottawa, Ontario, Canada. Figure 2 exhibits a picture of RTI's supported sorbent. Physical properties of the supported sorbent are listed in Table 1.

Figure 2: Picture of RTI's supported sorbent

Table 1: Supported sorbent properties

Property	Value
Bulk density	1.0 – 1.1 g/cc
AVG particle size	65 – 75 μm
Surface area	100 – 120 m^2/g
Physical strength (AR*)	0.77
Na_2CO_3 content	10 – 40 wt%

*AR refers to Attrition Ratio which is a relative measure of a material's attrition-resistance. Lower values represent stronger materials. A typical FCC catalyst – the basis for AR measurements – has an Attrition Ratio of 1.

Entrained-Bed Testing

CANMET, part of Natural Resources Canada, modified their circulating fluidized-bed combustor to accommodate CO_2 adsorption and regeneration testing using RTI's supported sorbent. RTI conducted seven full cycles (adsorption and regeneration) of entrained-bed tests at CANMET. Highlights of these tests are as follows:

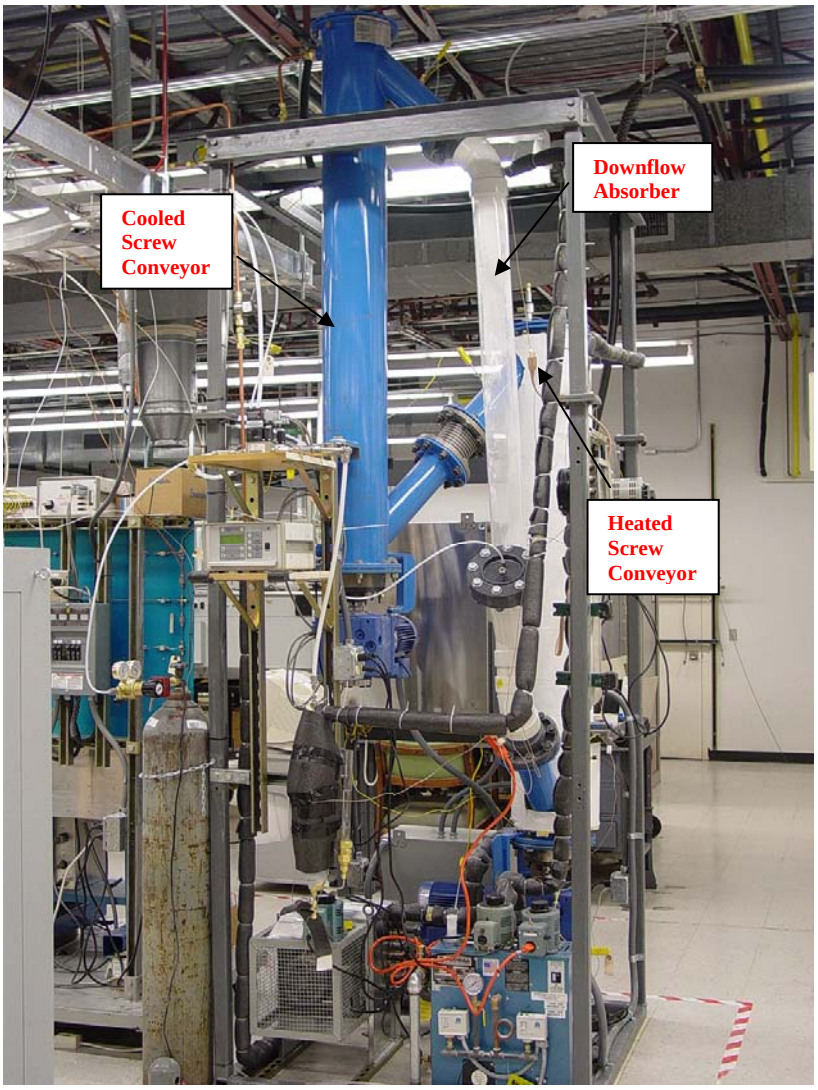
- RTI's supported sorbent, produced by a commercial catalyst manufacturer, was used
- > 90% CO_2 removal was demonstrated in the reactor
- The temperature rise (due to exothermic reaction) was limited to ~ 10ºC
- Sorbent reactivity was maintained over 7 cycles (consistent >90% removal)
- The sorbent was fully regenerated upon heating to 120ºC
- The sorbent showed negligible physical wear over 7 test cycles

Following CANMET testing, several engineering challenges remained and needed to be addressed in order to design a commercially-viable Dry Carbonate Process. These challenges included: designing a system to effectively use low grade heat (particularly from the power plant steam cycle) 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 reactors. To this end, RTI developed an alternative process design based on a co-current down-flow gas-solid contacting scheme and thermally-controlled mechanical screw conveyors. Much of the reactivity and attrition data collected from the CANMET entrained-bed testing was used to design and size an integrated bench-scale system.

Bench-scale Dry Carbonate System

An integrated unit, including two vertical screw conveyors and a down-flow adsorber, was assembled at RTI. The entire unit was assembled with all supporting brackets, steam and condensate piping and associated equipment, instrumentation, electronics, and electricity supply. Shakedown tests were performed at RTI using simulated flue gas. A picture of the integrated bench-scale system is displayed in Figure 3.

Figure 3: RTI's bench-scale, integrated CO_2 capture system



Process Advantages

The expected advantages of the Dry Carbonate Process (as compared to MEA processes) are as follows:

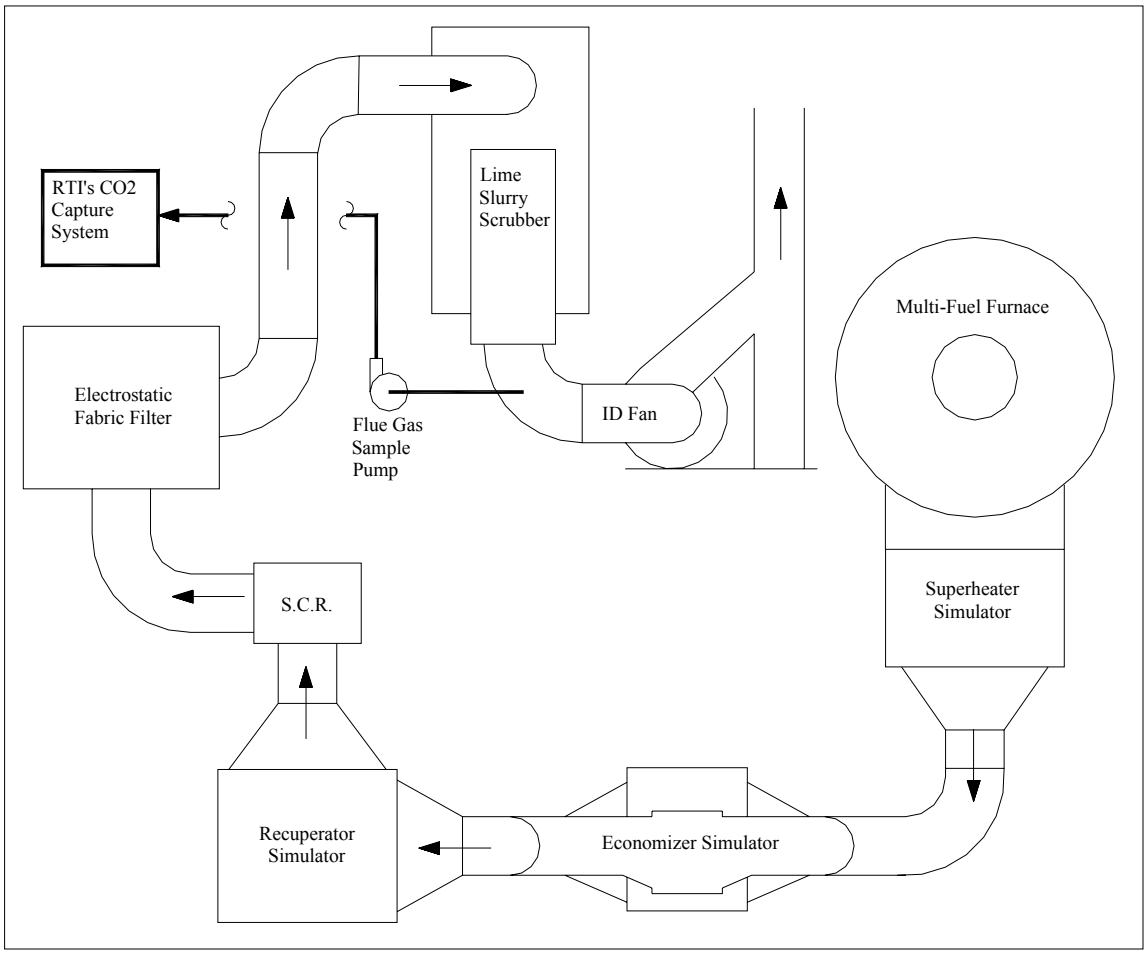
- Potential for more energy efficient CO_2 capture
    - lower total regeneration energy requirement than MEA
- Potential for lower CO_2 removal cost
    - low raw material cost
    - standard materials of construction
    - lower energy penalty
- Modest temperatures of operation
    - CO_2 adsorption at ~60°C ideal for flue gas from wet FGD
    - regeneration at ~120°C requires modest temperature swing
- Carbonate chemistry is well-known
- Non-hazardous and non-toxic raw materials
- Tolerance to contaminants in flue gas
- No hazardous waste generated

EXPERIMENTAL

Field Demonstration of RTI's Bench-scale Dry Carbonate System

RTI collaborated with ARCADIS U.S., Inc. to demonstrate the Dry Carbonate technology at an actual coal-fired combustion facility. ARCADIS is the U.S. EPA's on-site contractor responsible for the operation of the Multi-Pollutant Control Research Facility (MPCRF) at EPA's Air Pollution Prevention and Control Division (APPCD) in Research Triangle Park, NC. The MPCRF consists primarily of the following equipment and systems: a 4 MMBtu/hr multi-fuel furnace (gas, oil, and coal), thermodynamic load simulators, an electrostatically-enabled fabric filter, and a lime slurry wet scrubber. A diagram of the MPCRF and its components is shown in Figure 4.

Figure 4: Basic Schematic of EPA's MPCRF and Relative Location of CO_2 Capture System



The MPCRF is equipped with a flue gas cleaning system (FGCS) consisting of a selective catalytic reduction (SCR) system, an electrostatic fabric filter (ESFF), and a lime slurry wet scrubber. At its full firing rate the flue gas flow is roughly 1,000 SCFM.

The MPCRF combustor is sized so that viable multi-pollutant flue gas cleaning technologies may be tested, modeled, and scaled up for commercial applications. In addition, the combustor has temperature and gas velocity profiles reasonably close to commercial systems, such that combustor modifications and combustor sorbent-particle interactions may be coupled with cooler flue gas cleaning technologies to evaluate best combinations of combustion and flue gas cleaning technologies. The combustor is able to fire pulverized coal, distillate oil and/or natural gas at 2 to 4 million Btu/hr, yielding the noted flue gas flow at 300°F (150°C) when it enters the MPCRF's flue gas cleaning systems.

RTI's CO_2 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:

- Connected to 100 A, 3-phase, 208 V electrical service
- Insulated flue gas line leading to compressor
- Installed vent lines for "treated" flue gas and regeneration off-gas
- Installed piping for cooling water and steam boiler feed
- Connected drain lines for cooling water and steam condensate
- Installed piping for compressed air line

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 absorber. 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.

With the two systems integrated and running, several tests of the bench-scale CO_2 capture unit were conducted using desulfurized fossil fuel-derived flue gas. These tests were conducted using both natural gas- and coal-derived flue gas. The objectives of this field 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

In a typical test, flue gas was fed into the system at a measured flow rate and the inlet and outlet CO_2 concentrations were determined. After establishing a steady state in the system, the sorbent was introduced and changes in CO_2 concentration in the outlet gas were observed.

Under certain process conditions, CO_2 capture exceeded 90%. Overall, the system was operated for a total of 230 hours with fossil fuel-derived flue gas (130 hours of operation with natural gas derived flue gas and the balance with coal-derived flue gas).

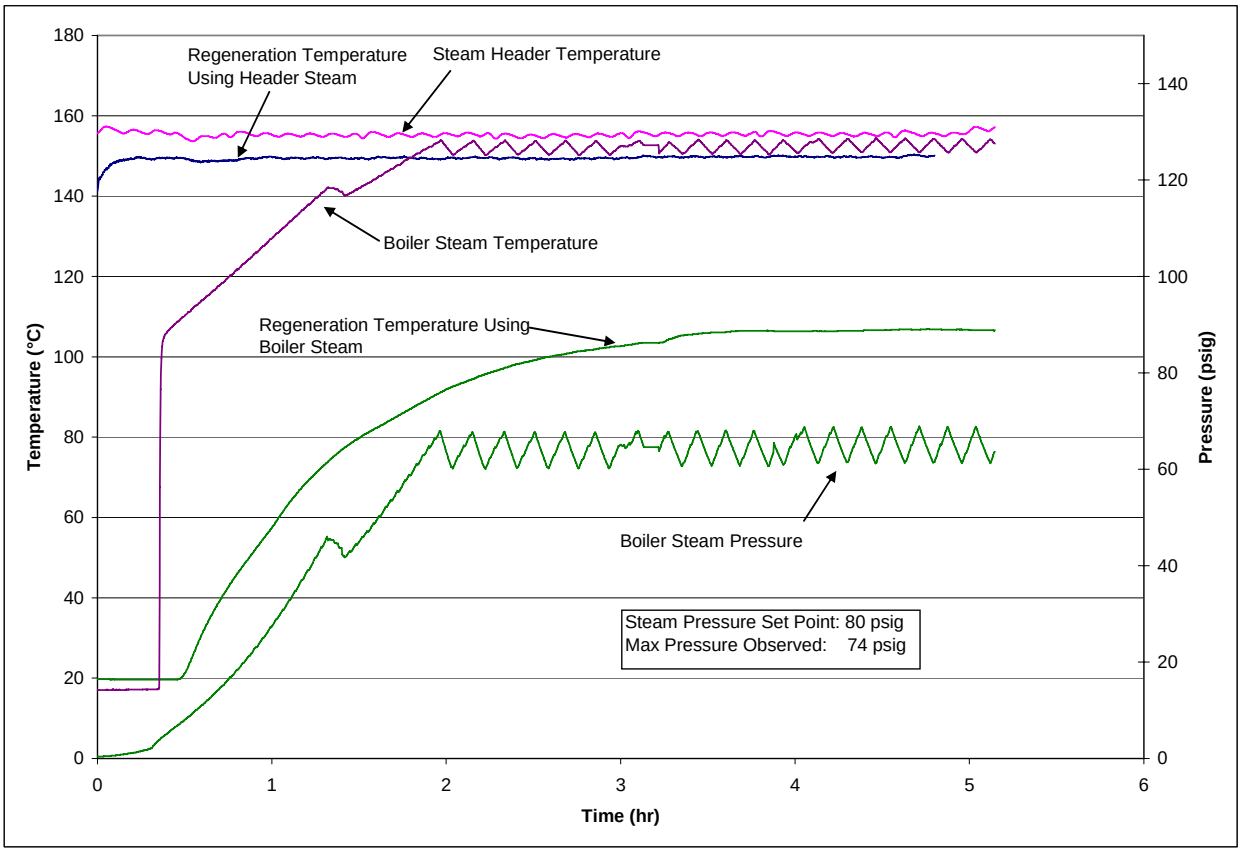
RESULTS AND DISCUSSION

Sorbent Regeneration Improvements

During field testing at EPA, the extent of regeneration of the sorbent was improved over that observed during previous RTI laboratory testing. The RTI bench-scale system is equipped with a 3 kW electric boiler that is able to provide steam of adequate temperature and pressure, but it can not provide an adequate volume (or amount) of steam for sorbent regeneration. While testing at EPA, steam was supplied by EPA's 80

psig steam header rather than by the original boiler. The temperature of the steam from the 80 psig steam header was relatively constant at 150˚–160˚C. A comparison of steam header and boiler regeneration parameters appears in Figure 5.

Figure 5: Comparison of regeneration parameters using 3 kW electric boiler and EPA's steam header



As shown in Figure 5, 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 5 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 CO_2 capture.

Natural Gas-derived Flue Gas Testing

The main goal of testing the Dry Carbonate system at EPA's MPCRF was to understand the interactions of coal-derived flue gas with RTI's carbonate-based sorbent. It is anticipated, however, that this technology is also applicable to CO_2 capture from natural gas-fired systems. Flue gas derived from the combustion of natural gas has fewer

chemical contaminants and no particulates, and is lower in CO_2 concentration than coal-derived flue gas.

Several tests were performed using natural gas-derived flue gas. Figure 6 shows a typical test result using natural gas-derived flue gas. CO_2 capture ranged from approximately 80% at high flue gas flow rates to 98.5% at lower flue gas flow rates.

Figure 6: RTI CO_2 Capture Test Unit - EPA Testing Natural Gas Combustion (CO_2 Concentration ~ 6 vol%)

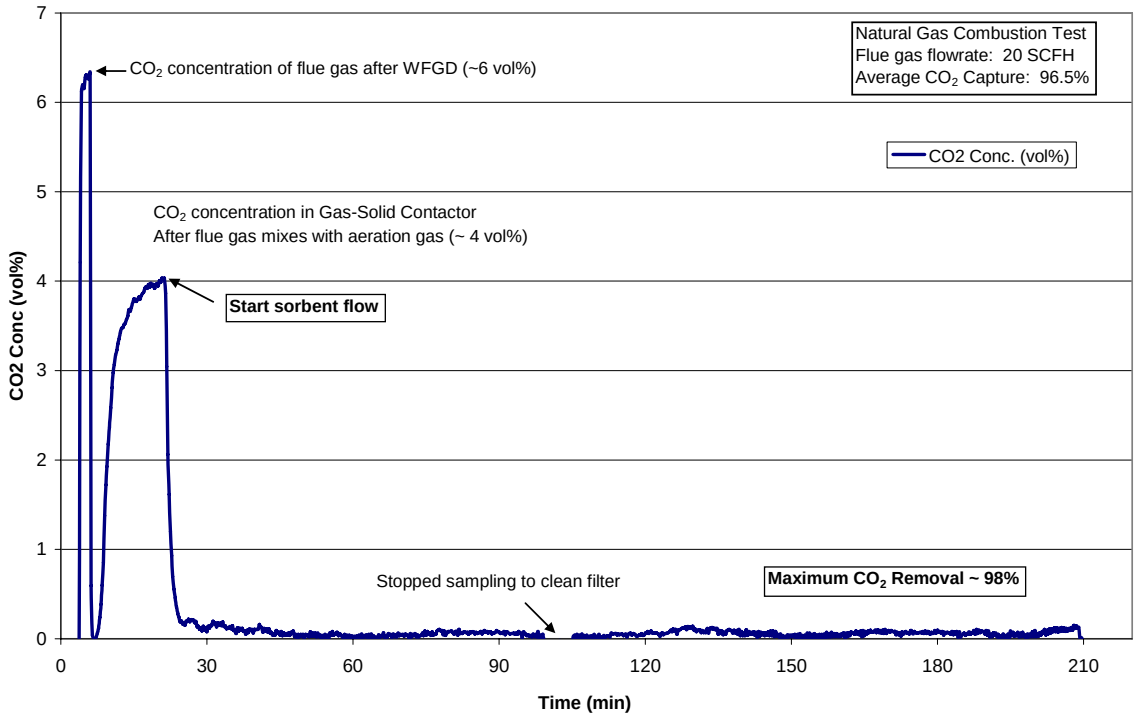


Figure 6 clearly shows that the Dry Carbonate system is capable of significant CO_2 removal from actual natural gas-fired flue gas. In addition, CO_2 removal of 90% and greater can be sustained over several hours of testing. The system was operated for a total of 130 hours with natural gas-derived flue gas.

Coal-derived Flue Gas Testing

Following a similar procedure as the natural gas tests, several tests were performed using coal-derived flue gas. Figures 7 and 8 show typical test results using coal-derived flue gas. CO_2 capture ranged from approximately 50% at high flue gas flow rates to 92.5% at lower flue gas flow rates.

Figure 7:

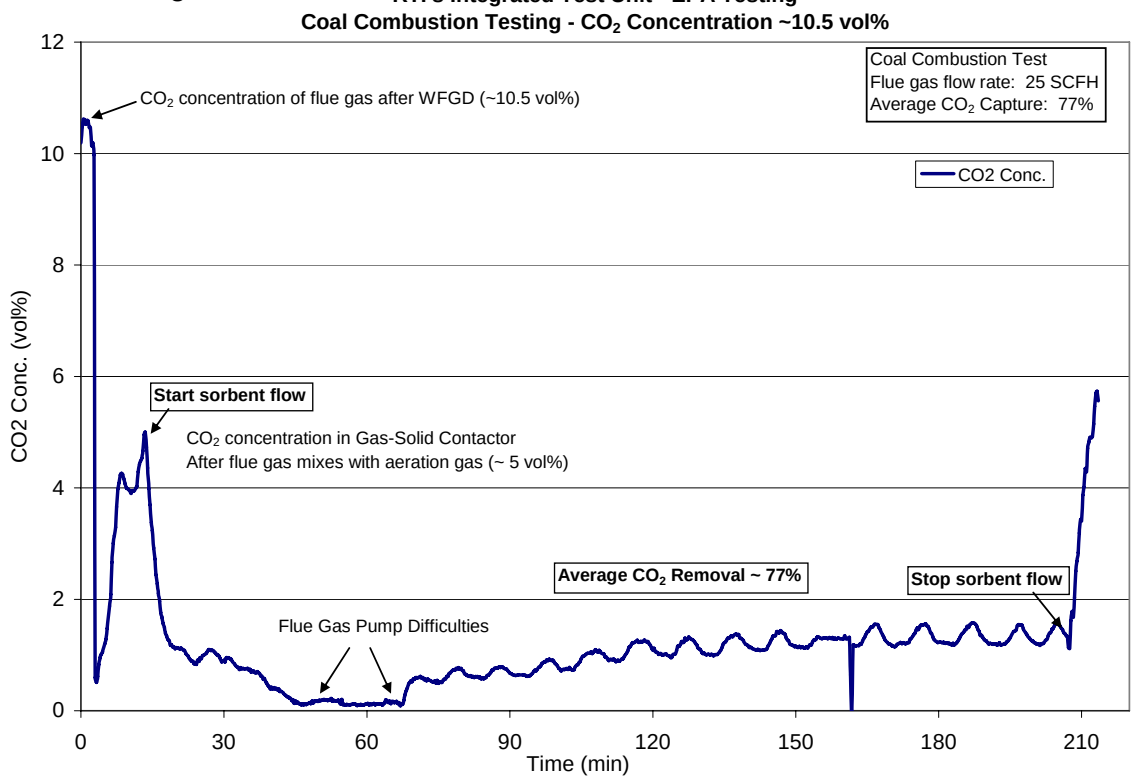
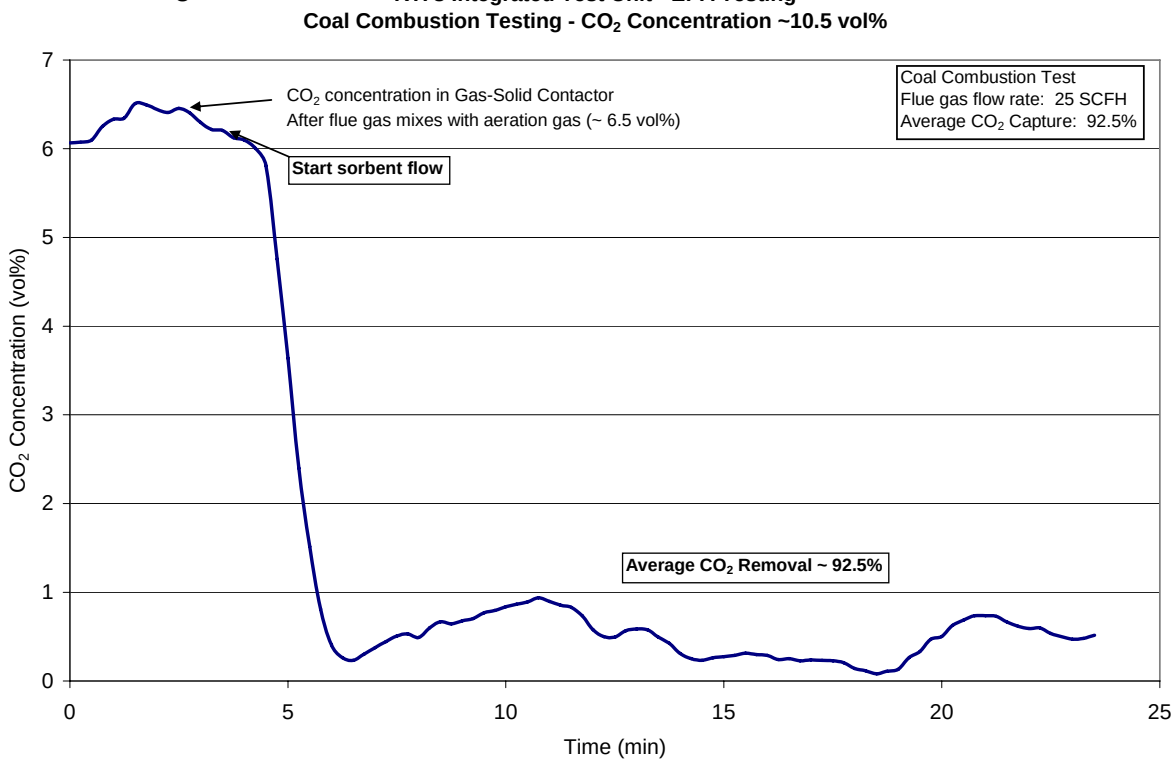


Figure 8:



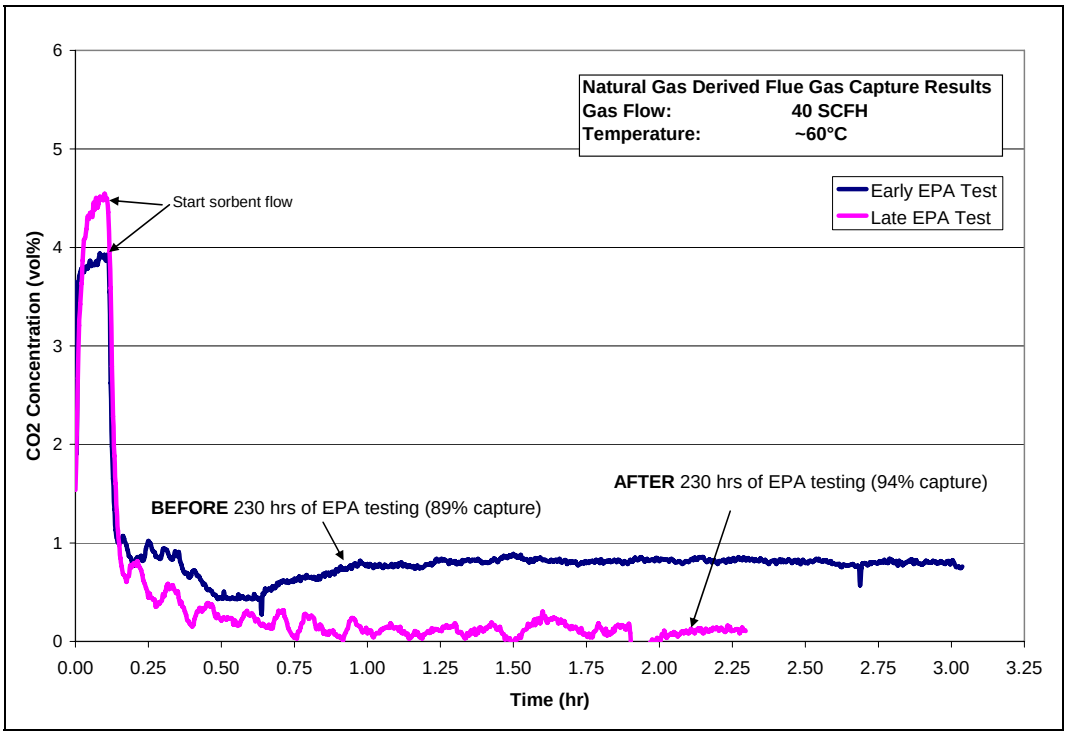
Similar to the natural gas combustion testing, Figures 7 and 8 clearly show that the Dry Carbonate system is capable of significant CO_2 removal from actual coal-fired flue gas. The system was operated for a total of 105 hours with coal-derived flue gas.

Evaluating Sorbent Performance Before and After Testing

One of the primary objectives of using coal-fired flue gas to test the CO_2 capture system and sorbent was to examine the effects contaminants in the coal-derived flue gas may have on the sorbent material. A permanent deactivation was expected of some of 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 SO_2 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 SO_2 and HCl, the low concentrations of these contaminants were expected to cause minimal deterioration to the sorbent activity. When the CO_2 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. The "improved" performance can be taken with a "grain of salt" since this may be attributable to inconsistencies in sorbent flow rates or other unknown factors. However, the point to be taken from this is that the sorbent performs consistently and shows no signs of deactivating. Figure 9 compares the CO_2 capture before and after exposure to coal-derived flue gas. In each case the flue gas is flowing at 40 SCFH, and screw drive motor control frequency at 20 Hz. The test gas was natural gas–derived flue gas. The "BEFORE" test was performed before any sorbent was exposed to coal-derived flue gas. The "AFTER" test was performed two months later after 105 hours of exposure to coal-derived flue gas.

Figure 9: Comparison of carbon dioxide capture before and after exposure to coal-derived flue gas.



Preliminary Economic and Technical Analyses

In an annual report prepared by RTI for the U.S. DOE, a preliminary economic evaluation of the Dry Carbonate Process was completed by following the DOE's *Carbon Capture and Sequestration Systems Analysis Guidelines*. These guidelines served as a reference for comparing the economic performance of a power plant with RTI's process installed to that of a power plant implementing amine-based (MEA) CO_2 capture and to a power plant without CO_2 capture. With the equipment and utility streams sized accordingly, estimates of the power performance, operating costs, and capital costs were made. These were preliminary estimates designed to get a "ballpark" feel for how a commercial Dry Carbonate Process compares to a MEA CO_2 capture system. The Dry Carbonate Process installed at a 500 MW "greenfield" coal-fired power plant shows promise to limit the increase in cost of electricity to less than 20%. A more detailed economic analysis is currently being conducted with the help of Electric Power Research Institute (EPRI) and will provide a more realistic estimate of the energy and cost improvement the Dry Carbonate Process offers over MEA technology. A qualitative review of the Dry Carbonate economic advantages is provided in Table 2.

Table 2: Qualitative Review of RTI's Economic Analysis Findings

Economic Improvement over MEA	Description
Lower steam turbine power de-rating	Dry Carbonate Process has lower total regeneration energy requirement; Additional novel heat integration improvements were assumed
Lower auxiliary power load	Less energy required to operate induced draft fans due to lower pressure drop
Lower capital costs	Modest temperatures of operation and non-corrosive reactants means standard equipment and materials of construction can be used
Lower reactive material costs	Dry Carbonate sorbent assumed to be more stable; initial sorbent charge and make-up costs are lower than amines

Continuing Research and Development

A new DOE-funded effort seeks to design, build, commission, and operate a "pre-pilot" unit of about 1-2 ton/day CO_2 capacity in a highly instrumented coal-fired power facility utilizing various coals (eastern and western) and lignites. This will be followed by extensive technical and economic evaluation of the process with particular emphasis on heat integration (to minimize operating costs and plant de-rating) and adaptability as a retrofit post-combustion technology to a typical coal-fired plant. The ultimate end products of the proposed project will be to develop a commercialization plan and to achieve a commitment from a U.S. utility to conduct a large-scale pilot-plant testing in Phase II of this project.

RTI has assembled a highly talented and experienced team to successfully execute the proposed effort. This team consists of ARCADIS U.S., Inc., Electric Power Research Institute, and ADA-ES. This team is designed to address various issues associated with successful development and commercialization of the proposed technology to meet DOE/NETL's near- and long-term goals.

SUMMARY

RTI's Dry Carbonate CO_2 capture system was successfully integrated into EPA's MPCRF. Process improvements were made to optimize regeneration. Tests were conducted using simulated, natural gas-derived, and coal-derived flue gases. The system was operated for a total of 230 hours using fossil fuel derived flue gas. The system has been demonstrated to run continuously for extended periods of time and has achieved greater than 90% capture of CO_2 under various process conditions. It appears that the sorbent remains active and sorbent performance does not diminish over the course of multiple (i.e. hundreds) cycles.

A comparative economic analysis of the Dry Carbonate Process, as applied to a baseline 500 MW_e coal-fired power plant, suggests that implementation of the Dry Carbonate

Process may be less energy intensive and less expensive than removal using an MEA liquid absorption system.

ACKNOWLEDGEMENTS

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