Carbon Dioxide Capture from Flue Gas Using Dry, Regenerable Sorbents

Quarterly Technical Progress Report

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Abstract

This report describes research conducted between July 1, 2006 and September 30, 2006 on the use of dry regenerable sorbents for removal of carbon dioxide (CO_2) from coal combustion flue gas. Modifications to the integrated absorber/ sorbent regenerator/ sorbent cooler system were made to improve sorbent flow consistency and measurement reliability. Operation of the screw conveyor regenerator to achieve a sorbent temperature of at least 120°C at the regenerator outlet is necessary for satisfactory carbon dioxide capture efficiencies in succeeding absorption cycles. Carbon dioxide capture economics in new power plants can be improved by incorporating increased capacity boilers, efficient flue gas desulfurization systems and provisions for withdrawal of sorbent regeneration steam in the design.

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1.0 Executive Summary

The objective of this project is to develop a simple and relatively inexpensive process to separate carbon dioxide (CO_2) as an essentially pure stream from a fossil fuel combustion system using a regenerable sorbent. The sorbents being investigated in this project are alkali carbonates, particularly supported sodium carbonate (Na_2CO_3) which is converted to bicarbonate (or an intermediate salt) through reaction with CO_2 and water vapor. The sorbent is regenerated to carbonate when heated, producing a nearly pure CO_2 stream after condensation of water vapor.

A bench-scale system has been built which incorporates a down-flow co-current contact absorber, a heated hollow screw conveyor, and a cooled hollow screw conveyor. In this quarter, improvements have been made to the screw conveyors and the gas sampling lines. The screw conveyors were modified to fix a maintenance problem and to improve the consistency of sorbent flow. A damaged shaft seal was replaced with a more durable seal and a porous metal air slide was installed at the inlet of the sorbent cooled screw conveyor to reduce or eliminate sorbent plugging problems. In addition, alternate particle filtration systems were tried in an effort to reduce plugging of the gas sampling line with sorbent fines.

A series of integrated system tests were conducted using a sorbent composed of sodium carbonate supported on a ceramic material. These tests suggested that heat transfer in the regeneration screw conveyor is adequate to bring the sorbent to a minimum temperature of 120°C.

Arrangements have been made to move the integrated unit to the U.S. Environmental Protection Agency’s (EPA's) combustion research facility in Research Triangle Park, NC for testing with a slip stream of actual desulfurized coal derived flue gas. Planning for utility hookups (power and cooling water), and coordination with the personnel responsible for operation of the combustor was completed in this quarter.

2.0 Introduction

Fossil fuels used for power generation, transportation, and non-utility sectors are the primary sources of anthropogenic CO_2 emissions. Although there are many potential approaches to limiting these greenhouse gas (GHG) emissions, including increased energy efficiency and use of carbon-free fuels, it is clear that CO_2 capture and sequestration will play an important role in mitigating the progress of global warming. In the near future, CO_2 capture efforts will likely focus on large stationary sources, such as fossil-fueled power plants, because these sources emit the largest quantities of CO_2 and will offer the benefits of economy of scale. It is for this reason that the United States Department of Energy’s (DOE’s) Carbon Sequestration Program, administered by the Office of Fossil Energy and managed by the National Energy Technology Laboratory (NETL), conducts and funds research to develop CO_2 capture and sequestration technologies.

The focus of this project is the development of a simple and inexpensive process to remove CO_2 from the flue gas of existing power plants (particularly coal-fired plants) using a dry, regenerable sorbent. This capture technology is based on the reversible reactions between CO_2 and sodium carbonate. Using a cyclic thermal-swing process, an essentially pure CO_2

stream can be removed from flue gas for subsequent sequestration or reuse. Capture of CO_2 from low-temperature flue gas using Na_2CO_3-based sorbents results in the reversible formation of sodium bicarbonate ($NaHCO_3$) and/or Wegscheider's salt ($Na_2CO_3 \bullet 3NaHCO_3$), as shown in Reactions 1 and 2:

Reaction 1.

$$Na_2CO_3(s) + CO_2(g) + H_2O(g) \leftrightarrow 2NaHCO_3(s) \qquad \left[\Delta H_r^O = -32.4 \text{ kcal/mol } CO_2\right]$$

Reaction 2.

$$Na_2CO_3(s) + 0.6\, CO_2(g) + 0.6\, H_2O(g) \leftrightarrow 0.4\left[Na_2CO_3 \bullet 3NaHCO_3(s)\right] \qquad \left[\Delta H_r^O = -32.5 \text{ kcal/mol } CO_2\right]$$

Both forward reactions (CO_2 absorptions) are exothermic. The equivalent reverse reactions (sorbent regeneration) are endothermic and produce equal molar quantities of CO_2 and H_2O. Condensation of H_2O from the regeneration product results in a pure CO_2 stream that is suitable for sequestration or reuse.

An integrated system has been constructed which incorporates a down-flow co-current absorber, a steam-heated screw conveyor/sorbent regenerator, and a water-cooled screw conveyor/sorbent cooler. An attrition-resistant supported sodium carbonate sorbent has been developed.

This report describes activities conducted between July 1, 2006, and September 30, 2006, by RTI International (RTI). Activities conducted this quarter include modifications to the screw conveyors to improve sorbent flow and testing of the integrated system. In addition, negotiations to conduct slip-stream testing at a combustion research facility were completed.

3.0 Experimental

3.1 Modifications and Improvements to the Screw Conveyors in the Integrated Unit

In the early stages of testing the integrated unit, RTI noticed that the CO_2 content in the "treated" gas coming from the absorber was higher than expected. It was determined that the additional CO_2 was coming in from the sorbent regenerator (i.e. following sorbent regeneration, the CO_2 and H_2O "off-gas" was carrying over into the sorbent cooler and, subsequently, the absorber). The diagnosed problem was that the venturi system designed to enable "off-gas" disengagement from the sorbent was not working effectively. This problem was corrected by installing a Laboport Model N86KTP vacuum pump to replace the venturi system.

The carbon dioxide analyzer used to measure the CO_2 content of the "treated" gas (and thus the CO_2 removal efficiency) was found to be very sensitive to changes in pressure at the measurement cell. Particulate build-up in the sampling tube resulted in an increased pressure drop, leading to decreased pressure and a negative bias in indicated CO_2 concentration readings.

The shaft seal located at the bottom of the heated screw conveyor failed due to wear associated with the accumulation of sorbent. The damaged seal is shown in Figure 1. 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.

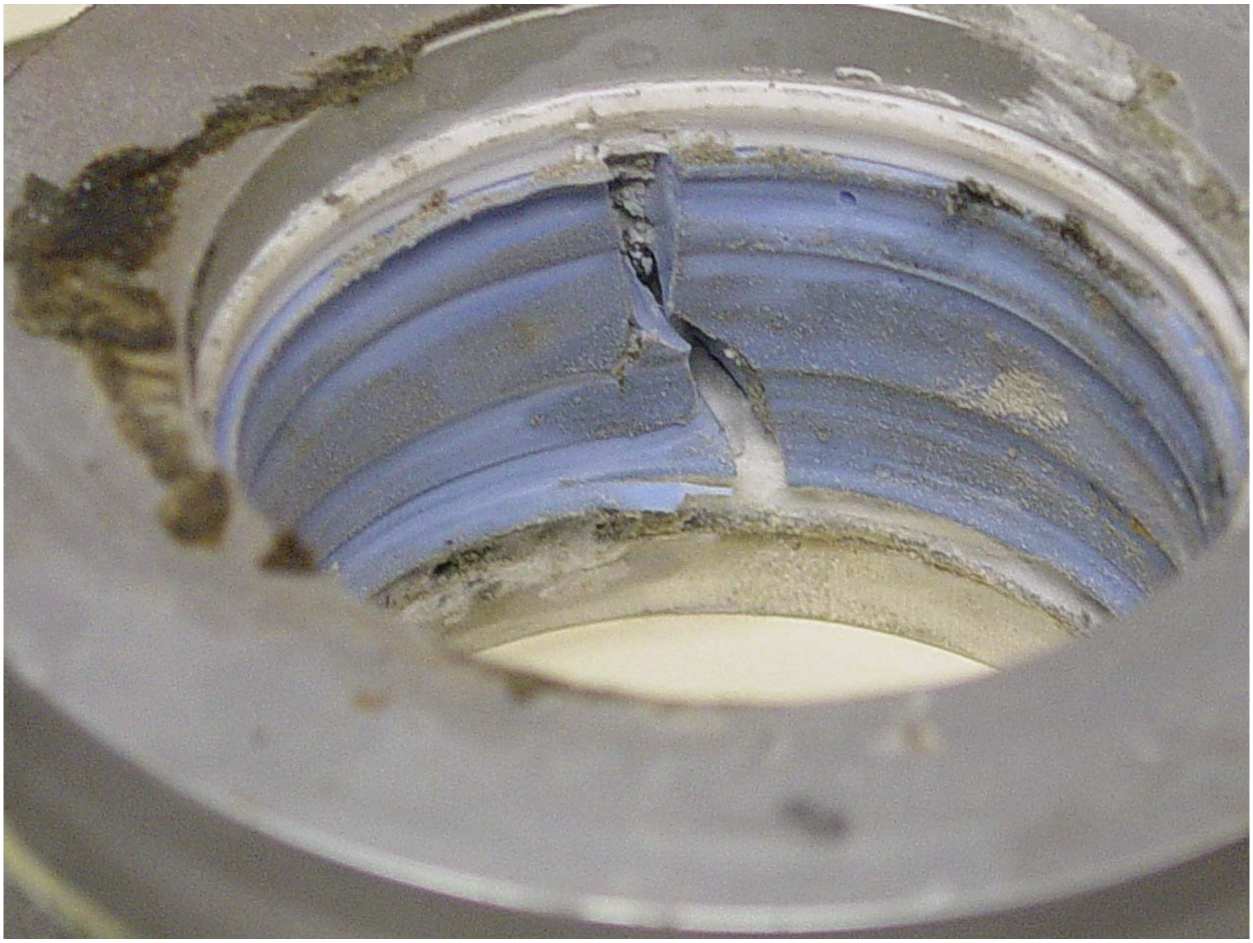

Figure 1. Regenerator Shaft Seal after Failure.

During several integrated unit tests, it was observed that circulated sorbent was accumulating at the inlet of the cooled screw conveyor, leading to eventual flow stoppage. This problem was eliminated through installation of a porous metal “air slide” at this point. The “air slide” allows the bulk of the sorbent to pass smoothly between the heated screw conveyor and cooled screw conveyor with very little hold-up.

With these modifications in place, two 8-hour periods of continuous solids circulation were completed this quarter. Note that these were two scheduled 8-hour tests intended to establish proof of flow consistency. Most of the tests conducted this quarter were shakedown tests of one or two hour duration to evaluate specific testing parameters.

4.0 Results and Discussion

4.1 Heat Transfer Capability of the Heated Hollow Screw Conveyor

Several tests were conducted to determine the heated screw conveyor's capacity for transferring heat to the sorbent particles. Of particular interest was observing the temperature of the sorbent bulk at the outlet of the heated screw conveyor. The heated screw conveyor was operated with 50 psig saturated steam as the heating medium. Sorbent was flowed through the absorber co-currently with simulated flue gas. The properties of the sorbent used, SCI-022806-1, are given in Green, et al., (2006). Sorbent temperature, measured at the outlet of the regenerator screw conveyor is shown in Figure 2. A slight variation in the steam pressure from the boiler was observed. This is also shown in Figure 2.

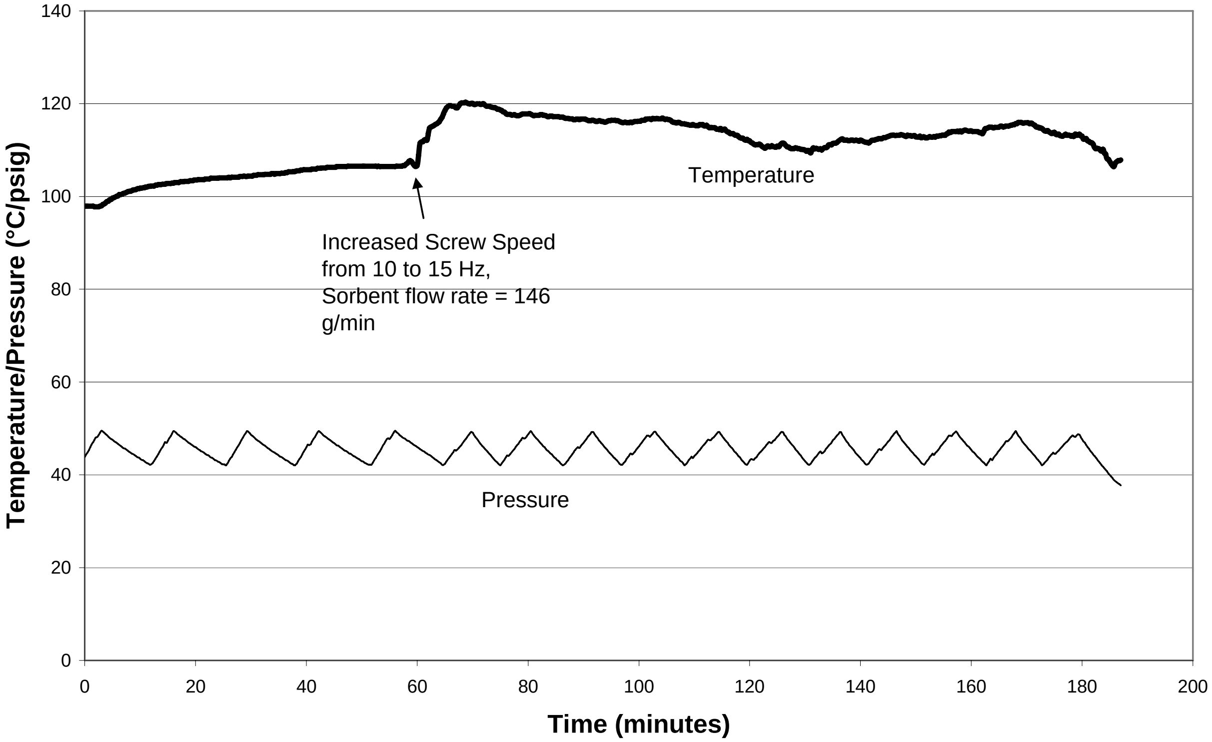

Figure 2. Temperature of Sorbent at Outlet of Regenerator Screw.

The sorbent entered the regenerator screw at approximately 28°C and reached 100 to 120°C under the noted process conditions. Steam pressure cycled between 43 and 50 psig. Previous research by RTI has shown that 120ºC is the minimum temperature that should be attained to expect full sorbent regeneration. It is evidenced that the noted process conditions in this test are able to heat the sorbent close to 120ºC, but additional steam pressure (higher saturation temperature) may be required to fully regenerate the sorbent.

4.2 Initial Carbon Dioxide Removal Tests (with Sorbent Regeneration)

RTI conducted several shakedown CO_2 removal tests during this quarter to confirm the effective operation of system components such as the sorbent regenerator, sorbent cooler, steam generator, and CO_2 analyzer. Data collected during the heat transfer test described in Section 4.1 is shown in Figure 3. CO_2 removals of up to 50% were obtained. It is believed that the observed CO_2 concentrations were skewed as a result of CO_2 leakage from the outlet of the regenerator screw into the absorber (as described in Section 3.1).

Another test was conducted to observe the operation of the steam generator and sorbent regenerator. Data from this test are shown in Figure 4. During the test, CO_2 removal increased from about 28% to about 43% as the sorbent to gas ratio was increased. It is theorized that decreased removal efficiencies resulted from incompletely regenerated sorbent. TGA testing of the "regenerated" sorbent used in this test confirmed RTI's assumption. TGA results showed an additional weight loss of about 5.5% upon heating the sorbent to 150°C. In subsequent testing, the pressure of the steam used to provide heat in the regenerator screw was increased to 60 psig (saturation temperature = 153°C).

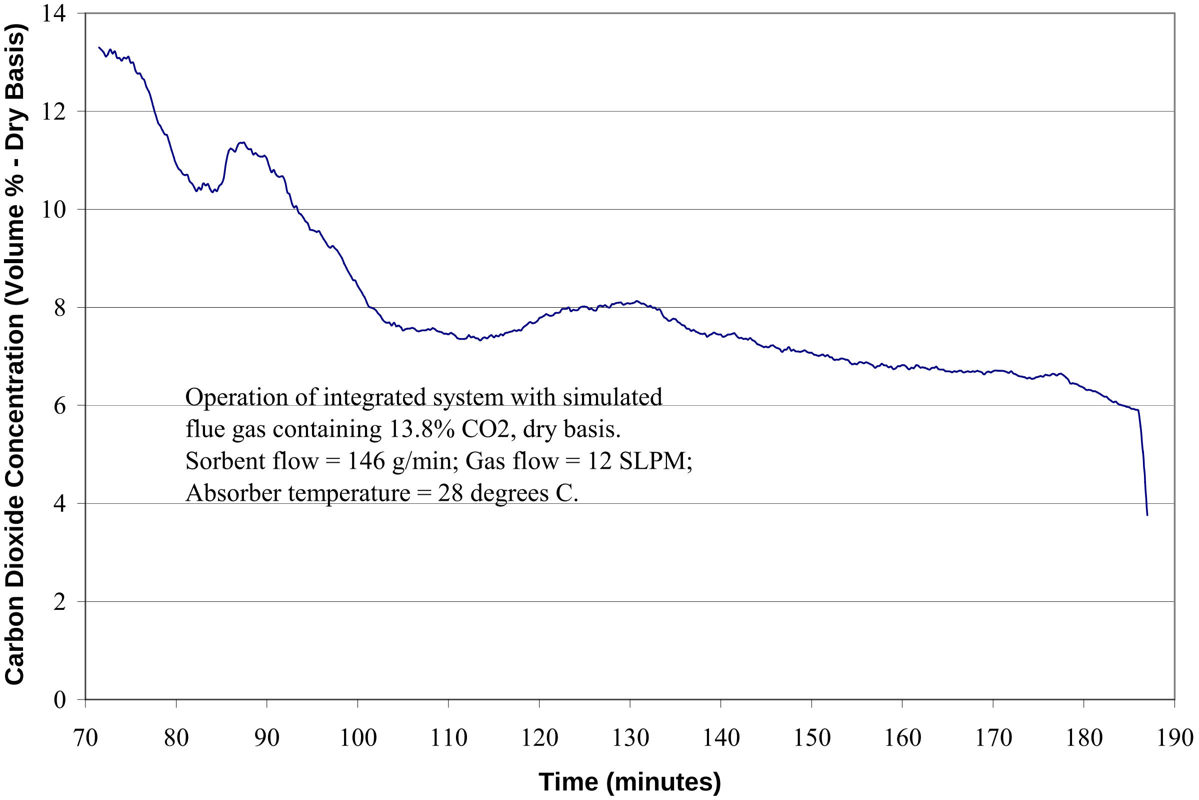

Figure 3. CO_2 Removal with Continuous Sorbent Regeneration at 110 to 120°C.

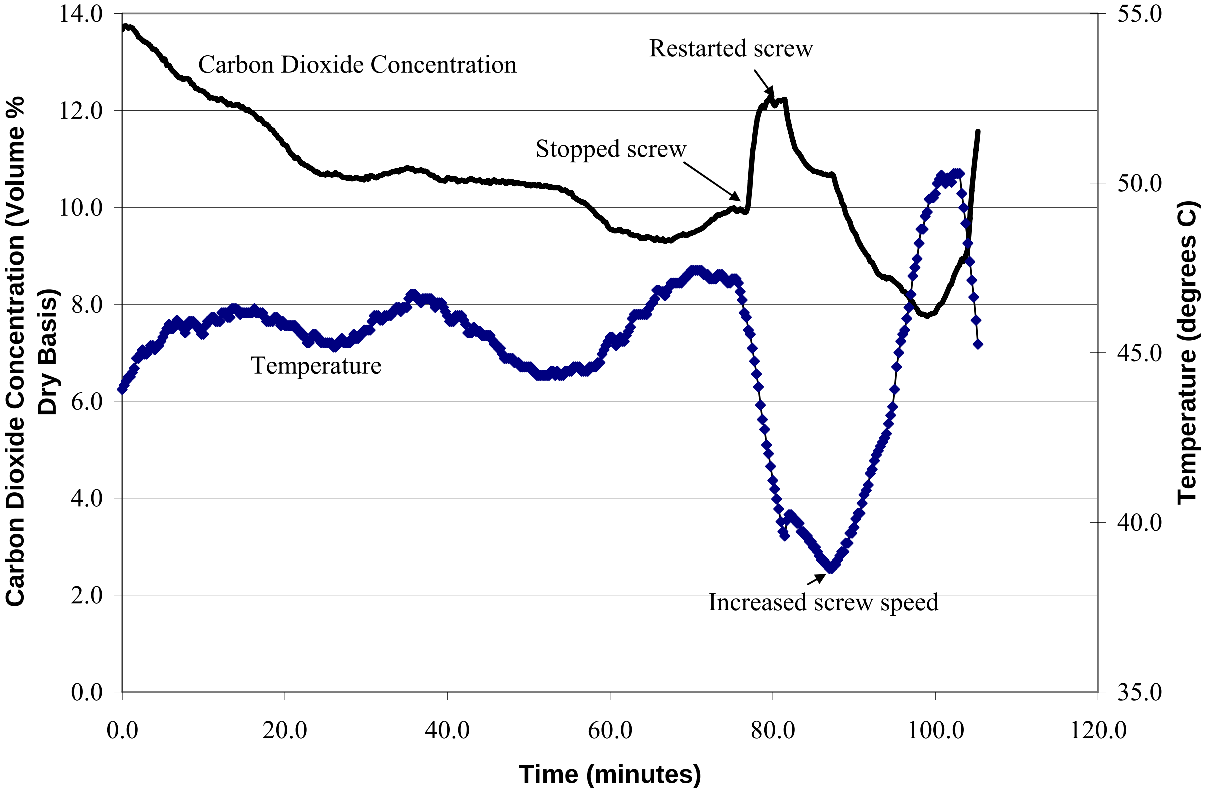

Figure 4. CO_2 Removal and Absorber Temperature with continuous Sorbent Regeneration at 110 to 120°C: Second Run.

An additional test was conducted after extensive regeneration of the sorbent at 120°C. This test immediately followed a number of system modifications and represents another shakedown CO_2 removal test. The modifications made to the system are as follows:

- A stack was added to the absorber gas outlet.
- A throttling valve was added between the regenerator outlet and the vacuum pump used to withdraw the CO_2/H_2O gas stream.
- A new filter arrangement was added to the absorber outlet gas sampling line.

The results of this test are shown in Figure 5.

The data shown in Figure 5 exhibit erratic readings probably caused by obstruction of the gas analyzer line. This line is subject to sorbent plugging which often leads to a negative bias in CO_2 concentration measurements. The carbon dioxide removal, as indicated, is inaccurate but is in the range of 30 to 50%. Additional modifications to the reactor to improve the gas sampling, i.e. more effective diversion of sorbent fines from the gas analyzer line are necessary and will be implemented in the coming quarter.

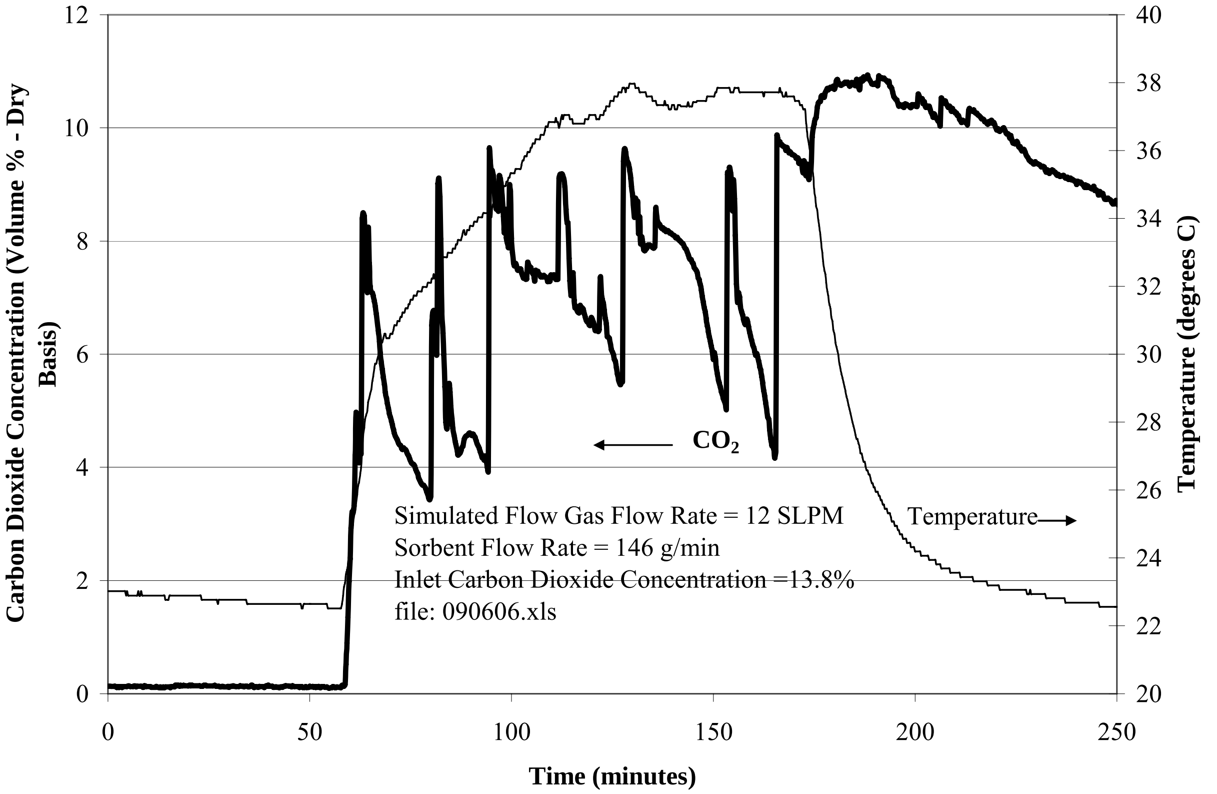

Figure 5. CO_2 Removal Following Continuous Sorbent Regeneration at 120°C: Intermittent Obstruction of Gas Analyzer Line.

5.0 Economic and Technical Analyses

5.1 Process Economics

In the most recent annual report prepared by RTI, an economic evaluation of the integrated "dry carbonate" process was completed following the DOE's System Analysis Guidelines (Nelson, et al, 2005). The key assumptions and design basis for this economic analysis are provided in Table 1. The key economic and power performance results are summarized in Table 2.

CO_2 removal from coal-fired power plant flue gas using the "dry carbonate" process may be less energy intensive and less expensive than removal using a monoethanolamine liquid absorption system. Based on the 2005 annual report, a comparative economic analysis of the processes, as applied to a baseline 498 MW_e plant without CO_2 removal, suggests that implementation of the dry carbonate process would result in an increase in the cost of electricity of 1.1 cents/kWh, in contrast to an increase of 3.2 cents/kWh for an MEA system. The 1.1 cents/kWh represents an increase in the cost of electricity of slightly less than 20%. This meets DOE goals of limiting the cost of electricity increase due to implementation of CO_2 capture to 20 percent for a coal-fired power plant (by 2012) as described in the DOE "Carbon Sequestration Technology Roadmap and Program Plan – 2006".

Table 1. Coal-fired Power Plant (w/ "Dry Carbonate" CO_2 capture installed) Assumptions and Analysis Design Basis (all dollar values are in 2005 dollars)

	Dry Carbonate Case
Location	East-West Region
Fuel	Illinois # 6 Coal
Base Plant	498 MW
CO_2 Removal Efficiency	90%
Capital Cost Year Dollars	2005
Capacity Factor (%)	65%
Levelized Capital Charge Factor (%)	14%
Project Book Life	20 years
Engineering Fees	6%
Process Contingency - Most plant components	0%
Process Contingency - CO_2 Capture system	20%
Project Contingency - Most plant components	10.6 - 26.5%
Project Contingency - CO_2 Capture system	40%

Table 2. Coal-fired Power (w/ "Dry Carbonate" CO_2 capture installed) Economic and Power Performance Results (all dollar values are in 2005 dollars)

	Dry Carbonate Case
Net Plant Power (KWe)	399,216
Plant Capital Requirement ($ X 1000)	$ 636,623
Dry Carbonate Capital Requirement ($ X 1000)	$34,500
Plant Operating Cost ($ X 1000/yr.)	$61,172
Dry Carbonate Operating Cost ($ X 1000/yr.)	$6,400
Capital c/kWh	3.9
Production c/kWh	2.7
Total c/kWh	6.6
$/ton CO_2 Avoided	23.9

5.2 CO_2 "Capture-Ready" Strategies in the Design of New Power Plants

The EIA estimates that between 2005 and 2030 the United States will require approximately 250 GW of new generation capacity to meet growing energy demand. Roughly 106 GW of this capacity will be met through the construction of new coal-fired power plants;

with the majority being traditional pulverized-coal power plants [EIA]. If these plants are constructed with no consideration of future retrofit for CO_2 capture, eventual retrofit costs may increase significantly. This problem can be alleviated if, during the initial design and construction phase, the plant is designed to be CO_2 "capture-ready". "Capture-ready" strategies will vary depending on the CO_2 capture technology to be employed. Optional considerations and strategies that could be introduced during the design and construction phase of a new plant in order to make it compatible with future installation of RTI's "dry carbonate" CO_2 removal process are shown in Table 3.

Table 3. Considerations in Design of "Capture-Ready" Power Plants

Equipment

- Specify larger, higher efficiency boiler to compensate for expected plant de-rating.
- Scale-up other plant equipment (pumps, fans, ductwork, etc) or at least allow for flexibility of re-sizing equipment in anticipation of additional load required after de-rating.
- Design the flue gas desulfurization system to allow for deeper desulfurization than is required by air pollution regulations (or leave available land/space to upgrade system in future).
- Construct additional ductwork or leave space available for future ductwork that will permit interfacing of the "dry carbonate" process to tie-in with the plant's ducting.
- Plan for tie-ins to the plant's steam cycle in order to allow extraction of low pressure steam for sorbent regeneration in the "dry carbonate" process.
- Plan for tie-ins to the plant's cooling water system to allow extraction of cooling water used in the "dry carbonate" process.

Land/Space

- Site plant close to feasible CO_2 market or storage location to allow for reduced transportation costs of CO_2 in future.
- Leave land/space available for "dry carbonate" process in strategic location.
- Leave land/space available for additional pumps, fans, compressors, etc. that will be needed in the plant due to the inclusion of the "dry carbonate" process.
- Leave land/space available for additional ductwork.
- Leave land/space available for upgrading of key plant equipment and systems (FGD, boiler, turbines, auxiliary electric plant, etc.).

6.0 Other Project Activities

The following is a list of other project activities that were carried out in this quarter:

- A presentation was made at the Twenty Third International Pittsburgh Coal Conference in September, 2006.
- A subcontract was finalized with ARCADIS Incorporated - the U. S. Environmental Protection Agency's on-site contractor. RTI and ARCADIS will work together to conduct a demonstration of the integrated system using a slip-stream of desulfurized coal-derived flue gas from EPA's combustion research facility in Research Triangle Park, NC. ARCADIS will be responsible for utility hookups for the integrated system which will be moved to EPA in November or December 2006.

7.0 Conclusions

Changes were made to the integrated carbon dioxide removal system to improve sorbent flow consistency and gas sampling reliability. These improvements included replacement of a damaged screw conveyor seal with a more abrasion resistant seal, addition of a porous metal shaft seal at the inlet to the cooled screw conveyor, and installation of a vacuum pump with a throttling valve to replace the venturi system previously used to withdraw the CO_2/H_2O gas stream from the outlet of the heated screw conveyor. Problems associated with insufficient CO_2 removal were traced to incomplete sorbent regeneration. Operation of the regenerator screw such that the sorbent reaches a temperature of greater than 120°C is expected to improve removal efficiency.

A technical analysis of CO_2 “capture-ready” considerations for new power plants was conducted. Strategies to make new power plant designs "capture-ready" should decrease retrofit costs and improve capture economics. Specific considerations include increasing boiler output, installing efficient flue gas desulfurization systems, and making provisions for withdrawal of regeneration steam and cooling water.

8.0 Future Work

The gas outlet sampling line from the absorber will be improved to avoid obstruction due to sorbent fines and potential measurement bias. A quality assurance project plan will be prepared for work at EPA's lab. An existing project health and safety plan will be revised to reflect operation with a slipstream of desulfurized coal-derived flue gas from EPA's combustor. The integrated system will be moved to the combustion research lab of the U. S. Environmental Protection Agency in Research Triangle Park, NC and interfaced with the EPA’s SO_2 scrubber.

9.0 References

Energy Information Agency, US Department of Energy (2006), "Annual Energy Outlook with Projections to 2030". (http://www.iea.doe.gov/oiaf/aeo/index.html)

Green, D.A., Nelson, T.O., Turk, B.S., Box, P., and Gupta, R.P. 2006. *Carbon Dioxide Capture from Flue Gas Using Dry Regenerable Sorbents*. Quarterly Technical Progress Report, RTI International.

Nelson, T.O., Green, D.A., Turk, B.S., Box, P., Li, W., Weber, A. and Gupta, R.P. 2005. *Carbon Dioxide Capture From Flue Gas Using Dry Regenerable Sorbents, Draft*. Annual Report, RTI International. October.