Carbon Dioxide Capture from Flue Gas Using Dry, Regenerable Sorbents

Quarterly Technical Progress Report

Reporting Period:
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Abstract

This report describes research conducted between July 1, 2005, and September 30, 2005, on the use of dry regenerable sorbents for removal of carbon dioxide (CO_2) from flue gas from coal combustion. A new batch of supported sorbent containing 10% sodium carbonate (Na_2CO_3) was obtained and characterized. Thermogravimetric analysis (TGA) testing confirmed that the Na_2CO_3 sorbent reacted with sulfur dioxide (SO_2) at temperatures between 40 and 160°C. Although the rate of reaction was more rapid at lower temperatures, these data suggest that SO_2 will not be released from the sorbent under expected sorbent-regeneration conditions.

Preliminary work has been conducted to establish the design specifications for a laboratory screw-conveyor sorbent regeneration/cooling apparatus. A plan for a scheduled pilot-scale test of a heated hollow-screw conveyor was developed. This test will be conducted at facilities of the screw conveyor fabricator. This test will confirm the extent of sorbent regeneration and will provide data to evaluate multi-cycle sorbent attrition rates associated with this type of processing.

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1.0 Executive Summary

The objective of this project is to develop a simple and 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 sodium carbonate (Na_2CO_3), which is converted to bicarbonate or to 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.

Work conducted this quarter included the preparation and characterization of a new batch of approximately 100 lbs of supported sorbent composed of 10% Na_2CO_3. This material was tested by thermogravimetric analysis (TGA) and found to react with sulfur dioxide (SO_2) at temperatures between 40 and 160°C. Because the reaction continued to proceed at 160°C, the SO_2 will not be released under expected sorbent-regeneration conditions.

A test plan was developed for pilot-scale testing of sorbent regeneration at the Therma-flite manufacturing facility in Benicia, California. This test plan focuses on confirming the ability of the heated-screw conveying system to regenerate the sorbent and determining the rate of sorbent attrition to be expected in multi-pass operation. The test is scheduled for October 2005. Preliminary specifications have been developed for a laboratory system composed of two hollow-screw conveyors for regenerating sorbent and cooling the regenerated sorbent for reuse.

2.0 Introduction

Fossil fuels used for power generation, transportation, and by non-utility sectors are the primary sources of anthropogenic CO_2 emissions. Although there are many potential approaches to limiting greenhouse gas (GHG) emissions, including increased energy efficiency and use of carbon-free fuels, it is becoming increasingly 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 will offer the benefits of economy of scale and the greatest benefits of CO_2 reduction from any one industry. 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 to develop a simple and inexpensive process to remove CO_2 from the flue gas of existing power plants using a dry, regenerable sorbent. This capture technology is based on the reversible reactions between CO_2 and supported sorbents. Using a thermal-swing cyclic process, an essentially pure 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.

This report describes activities conducted between July 1, 2005, and September 30, 2005, by RTI International (RTI). Activities conducted this quarter include TGA testing of a supported sorbent in an SO_2-containing gas; characterization of a new batch of supported sorbent; development of an experimental plan for a pilot-scale test to be conducted at the facilities of a screw conveyor manufacturer; and preliminary design of a hollow screw conveyor-based sorbent regeneration system.

3.0 Experimental

3.1 Production and Characterization of New Batch of Sorbent

A new batch of approximately 100 lbs of sorbent composed of 10% Na_2CO_3 on a ceramic support was prepared by a commercial catalyst manufacturer. This material will be reacted with CO_2 in a simulated flue gas and used for pilot-scale regeneration testing in a heated hollow-screw conveyor system. The surface area, porosity, and compact bulk density of the sorbent was determined for comparison to the previous batch.

3.2 Thermogravimetric Analyzer Tests of the SO_2-Na_2CO_3 Reaction

A series of six TGA tests was conducted to determine the temperature sensitivity of the reaction between SO_2 and the sorbent. Tests were conducted at 40, 60, 80, 120, and 160°C in an atmosphere of 148 ppm SO_2, 1.5% O_2, and balance N_2 for approximately 60 minutes.

4.0 Results and Discussion

4.1 Supported Sodium Carbonate Sorbent Characterization

The newly produced sorbent, SCI-090905-1, is composed of 10% Na_2CO_3 on a ceramic support. Sorbent properties are given in Table 1. Properties of the previous batch of sorbent (SCI-012705-1) that was used in the entrained bed tests (Green et al., 2005) are included for comparison. SCI-012705-1 contains 15% Na_2CO_3 by weight, thus it would be expected that SCI-090905-1 would have greater porosity and higher surface area, given the lower Na_2CO_3 content.

Table 1. Comparison of Supported Sorbent Properties

Sorbent	SCI-012705-1	SCI-090905-1
Na_2CO_3 Content, %	15	10
Surface Area, m^2/g	96.5	117
Bulk Density, g/cc	0.96	0.88
Porosimetry		
Total Intrusion Volume, cc/g	0.28	0.35
Total Pore Area, m^2/g	125	169
Median Pore Diameter (V), Å	84	80
Median Pore Diameter (A), Å	80	79
Average Pore Diameter (4V/A), Å	90	83
Bulk Density, g/cc	1.37	1.29
Apparent Density, g/cc	2.23	2.36
Porosity, %	38.4	45.3

The new material is more porous and has a greater surface area than the previously used material. This material (SCI-090905-1) will be used in the pilot-scale, heated hollow-screw conveyor regeneration tests planned for the next quarter. A downflow reactor test has also been conducted with this material. Details of this test are given in the annual report (Green et al., 2005).

4.2 Thermogravimetric Analyzer Tests of the SO_2 - Na_2CO_3 Reaction

The reaction of SO_2 with the sorbent was investigated using TGA. Expected reactions with the sorbent were

- Reaction 3

$$Na_2CO_3 + SO_2 \rightarrow Na_2SO_3 + CO_2$$

- Reaction 4

$$Na_2CO_3 + SO_2 + \frac{1}{2}O_2 \rightarrow Na_2SO_4 + CO_2.$$

A series of six TGA tests was conducted to determine the temperature sensitivity of these reactions. Data from the tests, which were conducted in an atmosphere of 148 ppm SO_2, 1.5% O_2, and balance N_2, is shown in Figure 1.

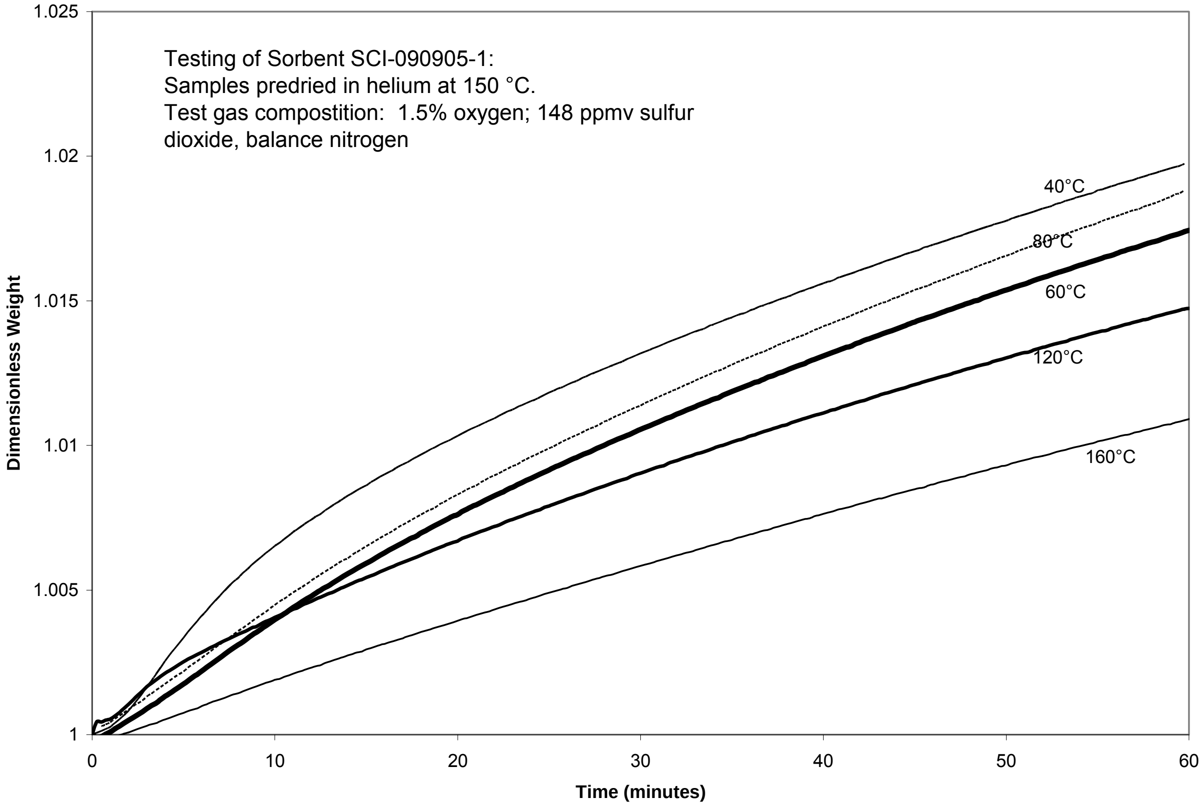

Figure 1. Reaction of SO_2 with supported Na_2CO_3 sorbent SCI-090905-1.

The data in Figure 1 indicate that although the rate at which the sorbent reacts with SO_2 generally decreases with increasing temperature, it proceeds at temperatures as high as 160°C. This suggests that the reaction will be irreversible at expected sorbent-regeneration temperatures of approximately 120°C. Note that although the data suggest that the reaction is slightly more rapid at 80°C than at 60°C, after the initial stages, this is unlikely to be significant and may represent a minor shift in the baseline of the instrument.

4.3 Development of Test Plan for Pilot-Scale, Heated Hollow-Screw Regenerator Trial

An experimental plan was developed for a pilot test to be conducted in October 2005 at the Therma-flite manufacturing facility in Benicia, California. The pilot-scale apparatus, shown in Figure 2, consists of a dual-screw conveyor. The apparatus is approximately 5 feet in length and has two hollow, heated screws housed in a metal jacket. The conveying speed is controlled by a motor, which in turn controls the rotational speed of both screw conveyors. The rotational speed can be varied from 0 to 8 revolutions per minute.

Figure 2. Pilot-test apparatus.

The plan for the test, scheduled in October, is given in Table 2.

Table 2. Test Plan for CO_2 Regeneration in Thermal Screw

1.) Regeneration is to occur at 260°F (127°C), this should be the set-point for the tempered heat transfer medium (oil).
(This is the same temperature of 35 psia saturated steam.)

2.) Before introducing the sorbent to the screw conveyor, begin circulating the heated oil through the system for at least one hour and confirm that the system has reached the regeneration temperature.

Once Through Testing

3.) The first pass through the regeneration screw is the most important. Allow all of the material (or at least as much as possible) to pass through the screw before proceeding to step 4.

Collect three samples in this "once through" test
Small samples of sorbent (3-4g each) should be collected near the beginning, middle, and end of the test
Label the samples to indicate the test (pass) # and relative time (i.e. beginning, middle, end)

Note the Following during the test (some parameters require noting every 5 to 10 minutes):

a.) Mean Residence Time ________________

b.) Exiting Temperature of Solid Material ________________

c.) Motor Speed ________________

d.) Vertical Pitch of Material Transfer ________________

e.) Mass of Material Introduced to Screw Inlet ________________

f.) Total Mass of Material Collected ________________
(Bulk Material Collected at Screw Outlet)

4.) Repeat the test three more times, taking samples, and noting the parameters. The motor speed and pitch should remain constant.

Continuous Cycle Testing

5.) After the "Once Through" Tests are complete, begin "Cycling Tests" by circulating the material through the conveyor several times (20-25 cycles or as many as time allows). Samples are only required once every few cycles and do not need to be collected at the beginning, middle, and end of the cycle as was done during the "Once Through" testing. A small (3-4 g) sample taken every 3rd cycle will be sufficient.
Label these samples with the time and cycle from which they were taken.

Return the Labeled Samples and as much of the material as possible to RTI International

4.4 Design of Heated Hollow-Screw Conveyor Sorbent Regeneration Apparatus

Design work is in progress for assembly of a laboratory screw-conveyor apparatus that will include both a steam-heated hollow screw for sorbent regeneration and a water-cooled hollow screw conveyor for sorbent cooling. A preliminary design has been developed in consultation with the manufacturer of the screw conveyors, and a plan for system fabrication and assembly in the RTI laboratories has also been developed. Design specifications for the screw conveyors are given in Table 3. A drawing and parts list for the dual-screw conveyor system are given in Figure 3 and Table 4.

Table 3. Design Specifications for Laboratory Screw Conveyor

HEATER DESIGN DATA:	
1. Product	: Sorbent material
2. Calculated Design feed rate	: 250 lb/hr
3. Bulk density	: 69 lb/cuft
4. Specific Heat	: Assume 0.25 Btu/lbF
5. Product inlet temperture	: 60° C
6. Product design outlet temperture	: 120° C
7. Heating medium	: 55 psi Steam @ 280° F
8. Material of construction	: Carbon Steel
9. Model selected	: HSH 6−6−2, Style A, (Single rotor)
10. Code Design	: ASME Section VIII, Division 1
COOLER DESIGN DATA:	
1. Product	: Sorbent material
2. Calculated Design feed rate	: 250 lb/hr
3. Bulk density	: 69 lb/cuft
4. Specific Heat	: Assume 0.24 Btu/lbF
5. Product inlet temperture	: 120° C
6. Product design outlet temperture	: 60° C
7. Cooling water inlet temperture	: 20.66° C
8. Cooling water outlet temperture	: 21° C
9. Cooling water flow	: 1.05 gpm
10. Material of construction	: Carbon Steel
11. Model selected	: HSC 6−6−2, Style A, (Single rotor)
12. Code Design	: ASME Section VIII, Division 1

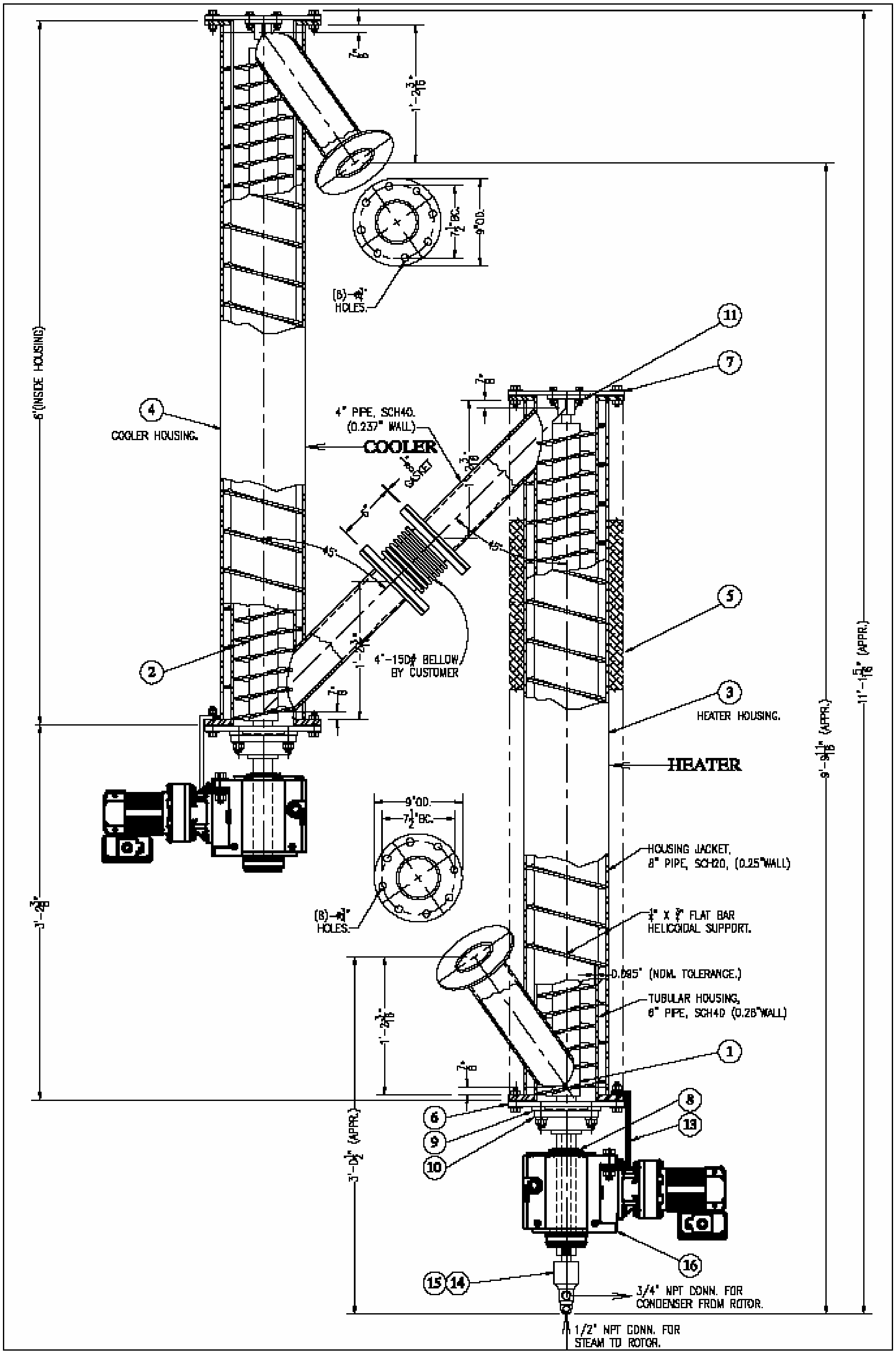

Figure 3. Double hollow-screw conveyor regenerator/cooler assembly.

Table 4. Parts List for Screw Conveyor System

REF. DWG.	ITEM	QTY	DESCRIPTION	MATERIAL
TLV-20767-C	1	1	HEATER ROTOR, HOLLOW DRIVE SHAFT, 5 7/8" NOM. OD. W/	CS.
			2" PITCH & 2" STEM PIPE. (R.H. ROTOR)	
TLV-20768-C	2	1	COOLER ROTOR, SOLID DRIVE SHAFT, 5 7/8" NOM. OD. W/	CS.
			2" PITCH & 2" STEM PIPE. (R.H. ROTOR)	
TLV-20769-C	3	1	HEATER HOUSING.	CS.
TLV-20770-C	4	1	COOLER HOUSING.	CS.
	5	1	1 1/2" THK. FIBERGLASS PIPE INSULATION W/ SELF-SEALING JACKET.	CS.
TLV-15939-A	6	2	END PLATE, (DRIVE END)	CS.
TLV-15940-A	7	2	END PLATE, (TAIL END)	CS.
	8	2	EXTERNAL RETAINING RING, # 5100-200.	STEEL
	9	2	PLATE SHAFT SEAL, "MARTIN" PART # CSP4 (2" BORE)	-
	10	2	FLANGE BALL BEARING, "MARTIN" PART # TEB4BB, (2" BORE)	-
	11	2	FLANGE BRONZE BEARING, (1" BORE)	-
TLV-15941-A	12	8	LIFTING/HOLDING LUG.	CS.
TLV-15942-A	13	2	GEAR REDUCER SUPPORT.	CS.
	14	1	ROTARY JOINT.	-
TLV-15943-A	15	1	ROTARY JOINT STOP. (NOT SHOWN)	CS.
	16	2	SHAFT MOUNTED GEAR REDUCER, "SUMITOMO" # LHYM02 2A	-
			100 YA 424, 1/4 HP, 424:1, 4.13 RPM, 2" HOLLOW BORE	-
			WITH TAPER BUSHING.	

5.0 Other Project Activities

Three interim reports were prepared that address work conducted to evaluate lithium silicate sorbents, multi-pollutant contaminant control approaches, and process economics within the DOE systems analysis framework. The content of these reports, as well as a discussion of downflow reactor experiments conducted this quarter, were incorporated in an annual report covering work completed during the period October 1, 2004, through September 30, 2005. This report was delivered in draft form to the DOE project manager.

6.0 Conclusions

A new batch of sorbent was prepared with a different Na_2CO_3 content and greater porosity and surface area.

TGA tests confirmed that SO_2 will react with Na_2CO_3 within the temperature window in which both the CO_2 sorption cycle (<80°C) and sorbent regeneration cycle (120 to 160°C) will occur. This means that SO_2 will not be released into the product CO_2 stream. Also, to the extent that SO_2 does react with the sorbent, it will be irreversibly deactivated.

7.0 Future Work

Additional downflow reactor tests will be conducted to optimize the absorption process for the Na_2CO_3-based sorbent and to obtain comparative data for unsupported, calcined Na_2CO_3.

Additional design work will be directed toward the laboratory-scale heated hollow screw regenerator/conveyor system.

A pilot-scale test of sorbent regeneration and sorbent attrition resistance will be conducted at the facilities of a heated screw conveyor manufacturer.

The draft annual report will be delivered in final form.

8.0 References

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