

# **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 October 1, 2004 and December 31, 2004 on the use of dry regenerable sorbents for removal of carbon dioxide from flue gas. Two supported sorbents were tested in a bench scale fluidized bed reactor system. The sorbents were prepared by impregnation of sodium carbonate on to an inert support at a commercial catalyst manufacturing facility. One sorbent, tested through five cycles of carbon dioxide sorption in an atmosphere of 3% water vapor and 0.8 to 3% carbon dioxide showed consistent reactivity with sodium carbonate utilization of 7 to 14%. A second, similarly prepared material, showed comparable reactivity in one cycle of testing. Batches of 5 other materials were prepared in laboratory scale quantities (primarily by spray drying). These materials generally have significantly greater surface areas than calcined sodium bicarbonate. Small scale testing showed no significant adsorption of mercury on representative carbon dioxide sorbent materials under expected flue gas conditions.

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## 1.0 EXECUTIVE SUMMARY

The objective of this project is to develop a simple and inexpensive process to separate CO<sub>2</sub> 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, and particularly sodium carbonate, which is converted to bicarbonate or to an intermediate salt through reaction with carbon dioxide and water vapor. The sorbent is regenerated to carbonate when heated, producing a nearly pure CO<sub>2</sub> stream after condensation of water vapor.

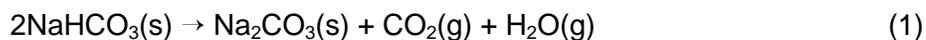
This quarter, four sorbents composed of 20 to 40% sodium carbonate on a support were prepared by spray drying, and an additional sorbent composed of 6.7% sodium carbonate on a support was prepared by an alternate procedure. These sorbents were prepared and characterized at RTI. Two additional sorbents composed of 15% sodium carbonate were prepared at a commercial facility. These two materials were tested in a 1-in diameter quartz fluidized bed reactor system to determine CO<sub>2</sub> capacity through multiple sorption/regeneration cycles. One material, tested through 5 cycles of sorption/desorption in an atmosphere of 3% water vapor and 0.8 to 3.0% carbon dioxide showed consistent reactivity over 5 cycles. Complete regeneration of the sorbent in pure nitrogen at temperatures of 100 to 180 °C was demonstrated.

This material, designated SCI 110504-2, was used as the recipe basis for the preparation of a large batch of approximately 20 kg. The preparation of this material marks the accomplishment of the milestone for this quarter, of developing an “optimized recipe for a supported carbonate-based sorbent with enhanced attrition resistance and chemical reactivity.” This large batch will be tested in a pilot-scale entrained-bed reactor at the CANMET Energy Technology Centre next quarter.

## 2.0 INTRODUCTION

Fossil fuels used for power generation, transportation, and by industry are the primary source of anthropogenic CO<sub>2</sub> emissions to the atmosphere. Much of the CO<sub>2</sub> emission reduction effort will focus on large point sources, with fossil fuel fired power plants being a prime target. The CO<sub>2</sub> content of power plant flue gas varies from 4% to 9% (vol), depending on the type of fossil fuel used and on operating conditions. Although new power generation concepts that may result in CO<sub>2</sub> control with minimal economic penalty are under development, these concepts are not generally applicable to the large number of existing power plants.

This study is based on the use of a dry, regenerable sorbent, such as calcined sodium bicarbonate (SBC), to remove CO<sub>2</sub> from flue gases. Sorbent regeneration produces a gas stream containing only CO<sub>2</sub> and H<sub>2</sub>O. The H<sub>2</sub>O may be separated by condensation to produce a pure CO<sub>2</sub> stream for subsequent use or sequestration. The primary reactions, based upon the use of SBC as the sorbent precursor and sodium carbonate as the reaction product are:



and



Reaction (1) releases  $\text{CO}_2$  and regenerates the sorbent, while Reaction (2) is used to capture  $\text{CO}_2$ . Other solid products, intermediate between sodium carbonate and sodium bicarbonate, may also be produced under the anticipated reaction conditions. An intermediate compound,  $\text{Na}_2\text{CO}_3 \cdot 3\text{NaHCO}_3$ , known as Wegscheider's salt, forms at the reaction conditions of interest. The corresponding reactions for Wegscheider's salt are represented by Reaction (3).



The carbon dioxide capture reaction is exothermic and the sorbent regeneration reaction (calcination) is endothermic, and takes place at a slightly higher temperature. The sorbent can be recycled numerous times. Traces of  $\text{SO}_2$  and  $\text{HCl}$ , which may be present in desulfurized flue gas from coal-fired power plants, will react irreversibly with the sorbent.

This report describes activities conducted between October 1, 2004 and December 31, 2004 by RTI. Activities conducted this quarter include development of improved supported sorbents, multicycle fluidized bed testing of supported sorbents, determination of sorbent properties and development of a test plan for pilot-scale transport reactor testing.

### **3.0 EXPERIMENTAL**

#### **3.1 Fluidized Bed Testing of Supported Sorbents**

Two sorbents were subjected to cyclic testing in a previously described (Green, et al., 2003) laboratory fluidized bed reactor system which was subjected to slight modifications. A 1-inch diameter quartz fluidized bed reactor with a total length of 48-in was used. A coarse quartz frit is fixed in roughly the middle of the reactor. The two ends of this quartz reactor are flanged, and a set of metal flanges is attached to seal the inlet and outlet process piping. Most of the length of the reactor is surrounded by a 3-ft clamshell furnace with a single zone furnace. The reactor is aligned to place the center of the sorbent bed supported on the coarse quartz frit at roughly the middle of the furnace's single heating zone. The heating control system uses the temperature from a thermocouple inserted through the upper flange into the center of the sorbent bed.

The feed system for this reactor system begins with a pair of mass flow controllers (MFCs) for metering in carbon dioxide and nitrogen. The gas from the MFCs flows into the lower inlet of the liquid vaporizer system which is heated externally with heat tapes and internally with a small heating rod. Liquid water is fed into the vaporizer with a syringe 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 is fed through a 1/4-inch stainless steel tube into the heated zone of the reactor below the coarse quartz frit through bottom flange. The gas fluidizes the sorbent bed, exits the reactor through the top flange and passes through a nondispersive infrared carbon dioxide monitor. The reactor system is shown schematically in Figure 1.

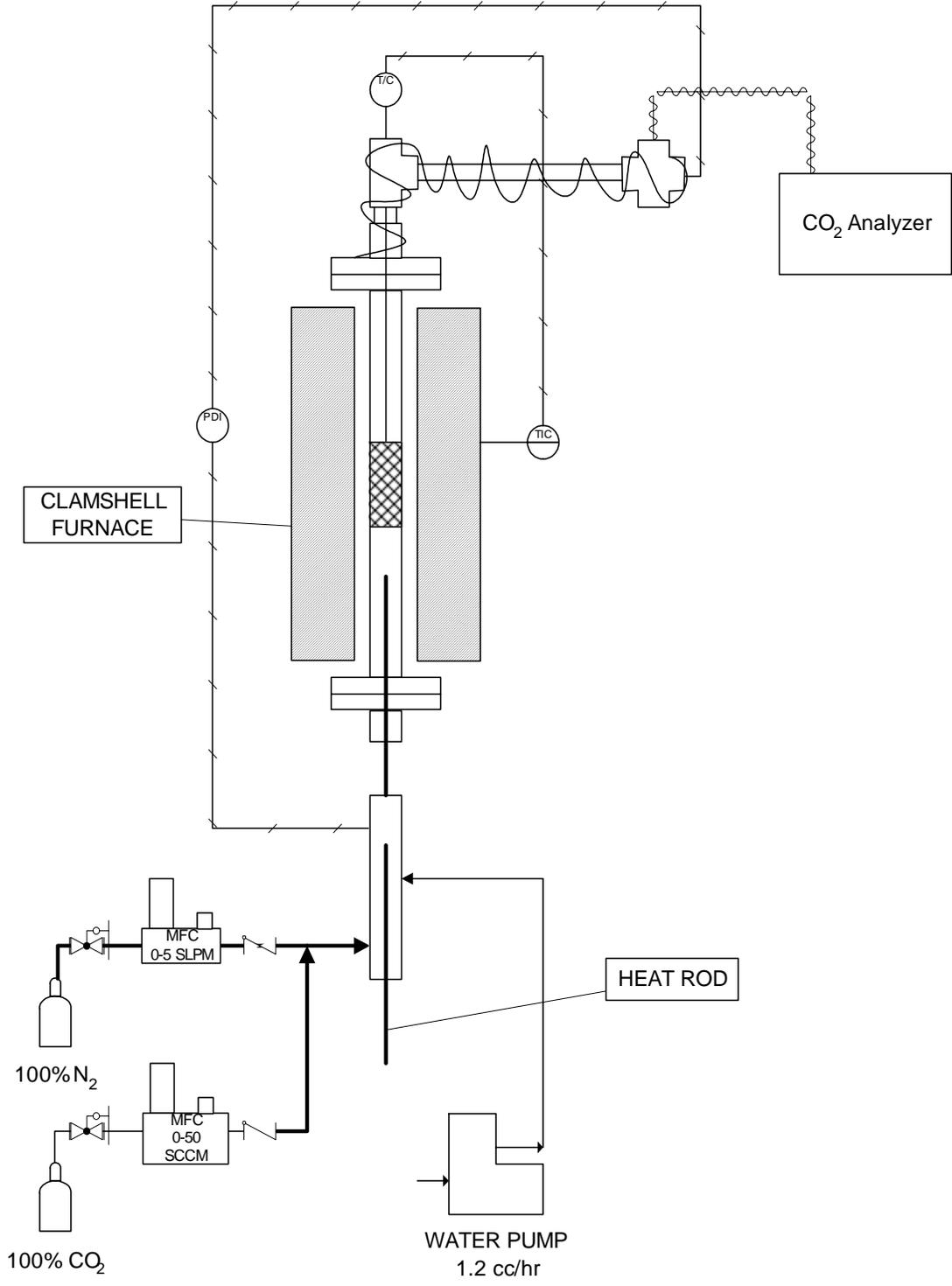


Figure 1. Quartz reactor

Both of the sorbents tested this quarter were composed of approximately 15% sodium carbonate on an inert support. Sorption took place in an atmosphere of 3% water vapor and 0.8 to 3.0% carbon dioxide (balance nitrogen) at a nominal temperature of 60°C. Regeneration took place in nitrogen. Carbon dioxide uptake was monitored by integrating the CO<sub>2</sub> flux during the regeneration cycle. One sorbent was tested through 5 sorption/regeneration cycles; the second was subjected to single cycles of sorption and regeneration.

### **3.2 Sorbent Preparation**

Four sorbents composed of 20 to 40% sodium carbonate on a support were prepared by spray drying, and one sorbent with a composition of 6.7% sodium carbonate on a support was prepared by an alternate procedure. These sorbents were prepared and characterized at RTI. Two additional sorbents composed of 10 to 15% sodium carbonate were prepared at a commercial facility. The BET surface areas and Davison attrition indexes were determined for selected sorbents. The carbonation activities were evaluated by thermogravimetric analysis (TGA). Carbonation activities of two previously prepared sorbents were also determined this quarter.

### **3.3 Mercury Adsorption Testing**

RTI undertook a study to determine if supported sodium carbonate-based sorbents are likely to adsorb mercury. Samples of approximately 0.5 g of material were exposed for 30 minutes to a nitrogen stream containing 460 micrograms of elemental mercury 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 mercury content using a Milestone DMA-80 direct mercury analyzer. To verify a material balance, the quality assurance measures included blank runs, and analyses of "backup" cartridges of a known mercury sorbent.

Three different formulations were tested: 20% sodium carbonate on alumina, 40% sodium carbonate on alumina, and 20% sodium carbonate on a silica-containing support. An existing small scale screening apparatus, shown in Figure 2 was used for this study.

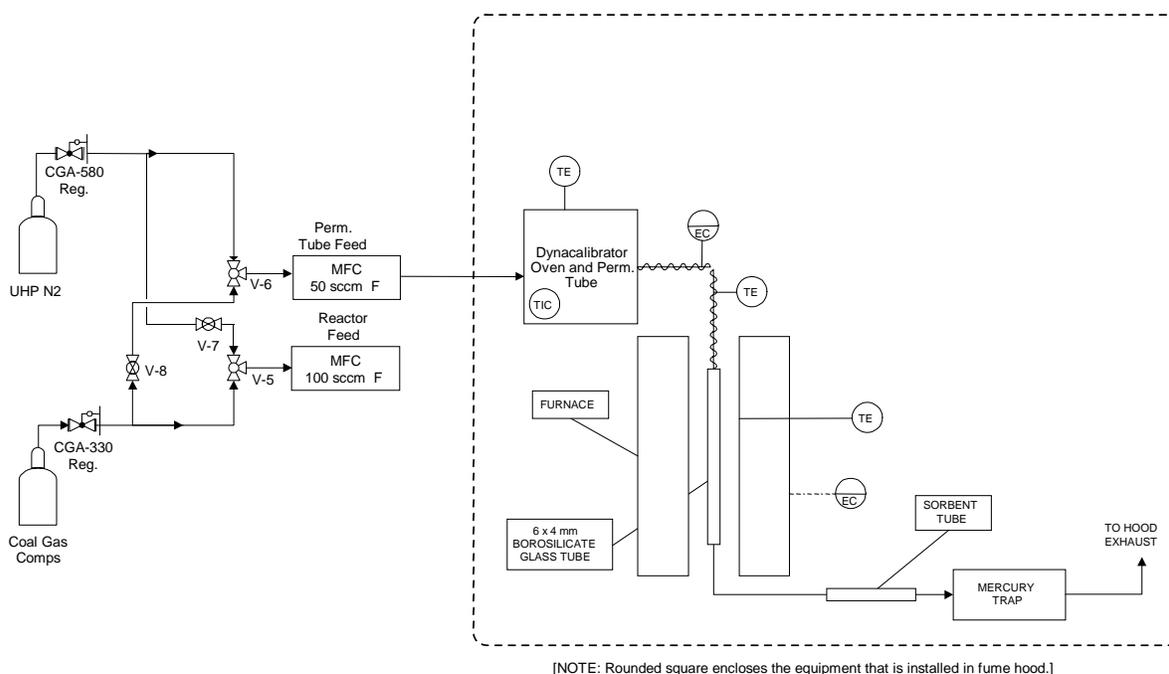
The dotted line in Figure 2 indicates equipment that was installed in a fume hood. Electronic mass flow controllers (MFC) established the flow rate of N<sub>2</sub> across the mercury vapor permeation tube housed in a temperature controlled (TIC) Dynacalibrator oven. Thermocouples (T) were placed to monitor the heat tracing of the process lines. Heat tracing temperature was controlled with variable transformers (EC).

## **4.0 RESULTS AND DISCUSSION**

### **4.1 Cyclic Fluidized Bed Testing**

#### **4.1.1 Five-cycle Testing of SCI-110504-2**

A sorbent (SCI-110504-2) composed of 15% Na<sub>2</sub>CO<sub>3</sub> on an inert support was subjected to 5 cycles of sorption and regeneration in the quartz reactor system. The reactor was loaded with 35 g of sorbent leading to an unexpanded bed depth of 3 in, and a height to diameter ratio of



**Figure 2. Small scale mercury adsorption screening apparatus**

approximately 3. The first four sorption cycles were conducted by fluidizing the sorbent in an atmosphere of 3.0% carbon dioxide, 3.0% water vapor (balance nitrogen). For the fifth sorption cycle, the carbon dioxide concentration was decreased to 0.8% carbon dioxide with the water vapor content held at 3.0%. All sorption tests were conducted at  $60 \pm 2^\circ\text{C}$ .

Breakthrough curves for the five sorption cycles are shown in Figure 3. The dotted lines represent the carbon dioxide concentrations on the reactor influent gas. A curve showing the carbon dioxide concentration in the absence of water vapor, representing the lag between gas introduction and the carbon dioxide monitor is also shown.

The flat portion at the beginning of the curves shows essentially 100%  $\text{CO}_2$  capture following the start of  $\text{CO}_2$  flow. Sorption was effectively complete when the carbon dioxide concentration of the reactor exit gas was equal to that of the reactor inlet gas. The gas was then switched to 100% nitrogen and the bed was heated to regenerate the sorbent. Sorbent regeneration was monitored by the concentration of carbon dioxide in the reactor exit gas, as shown in Figure 4. In this regeneration cycle, the furnace setpoint which controlled the bed temperature was progressively increased as indicated in Figure 4. The sorbent was considered to be completely regenerated when the carbon dioxide concentration of the reactor exit gas reached zero. Note that the mass of carbon dioxide desorbed can be calculated from the flow rate and the area under the concentration curve.

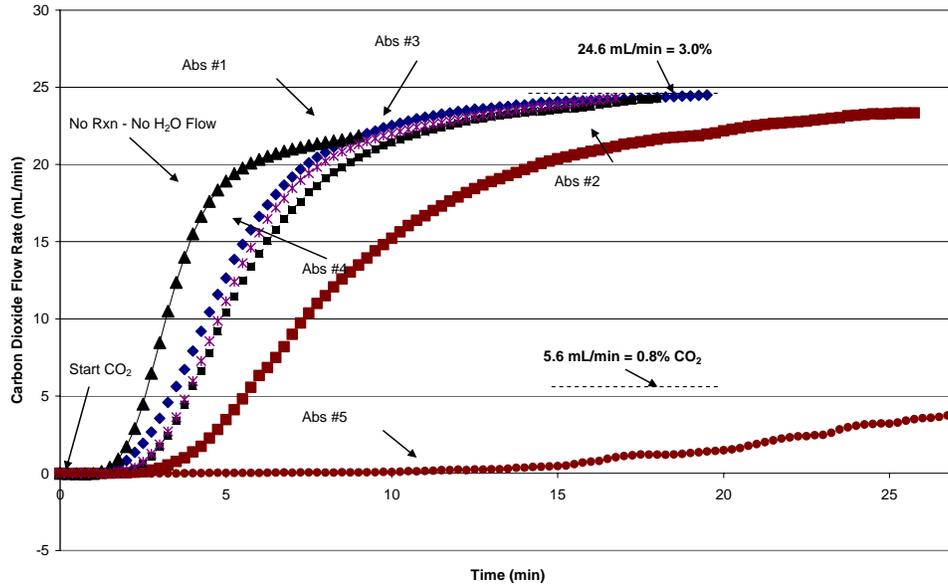


Figure 3. Comparison of Carbon Dioxide Sorption Breakthrough Curves for 5-Cycle Test of SCI 110504-2

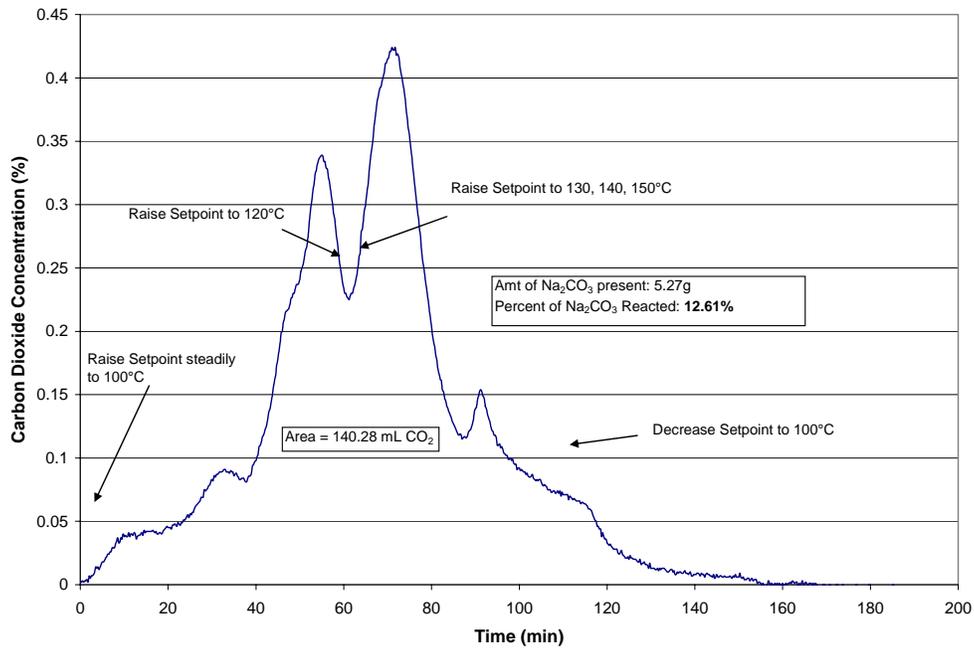
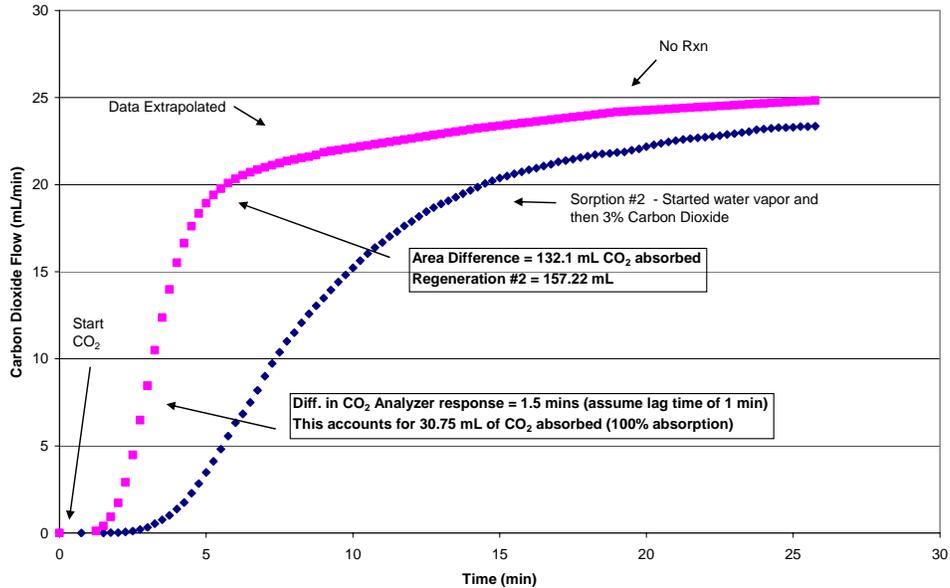


Figure 4. Sorbent SCI 110504-2 : Regeneration Cycle #1

The carbon dioxide measured in the reactor exit gas during the second sorption cycle is shown in Figure 5. The carbon dioxide analyzer response for the system in the absence of a reaction (i.e., when no water vapor is present in the reactor influent gas) is shown for comparison purposes. Adjusting for this analyzer delay, the mass of carbon dioxide reacted is calculated as the area between the two curves.



**Figure 5. Sorbent SCI 110504-2 : Sorption Cycle #2**

Data from the second regeneration cycle is shown in Figure 6. The furnace setpoint was increased as indicated on the figure until the carbon dioxide concentration of the reactor exit gas was approximately zero. An independent measurement of the carbon dioxide reacted in the preceding sorption cycle is provided by the integration of the regeneration curve. Note the calculation of 157 mL of carbon dioxide evolved in the regeneration exceeds the calculation of 132 mL integrated from Figure 5. This reflects additional carbon dioxide reacted after the output of the carbon dioxide analyzer became indistinguishable from what would be predicted in the absence of reaction.

The carbon dioxide measured in the reactor exit gas during the third sorption cycle is shown in Figure 7, analogously to the presentation in Figure 5. An estimated 32 mL of carbon dioxide was reacted, as calculated from the analyzer baseline. Note that upon regeneration following the third sorption cycle, an estimated 132 mL of carbon dioxide was evolved.

A fourth cycle of sorption and regeneration was conducted similarly to the first three cycles. Following the fourth regeneration, a fifth sorption cycle was conducted in a atmosphere of 0.8% carbon dioxide and 3% water vapor (balance nitrogen). Data from this cycle are shown in Figure 8, and data from the fifth regeneration cycle are shown in Figure 9.

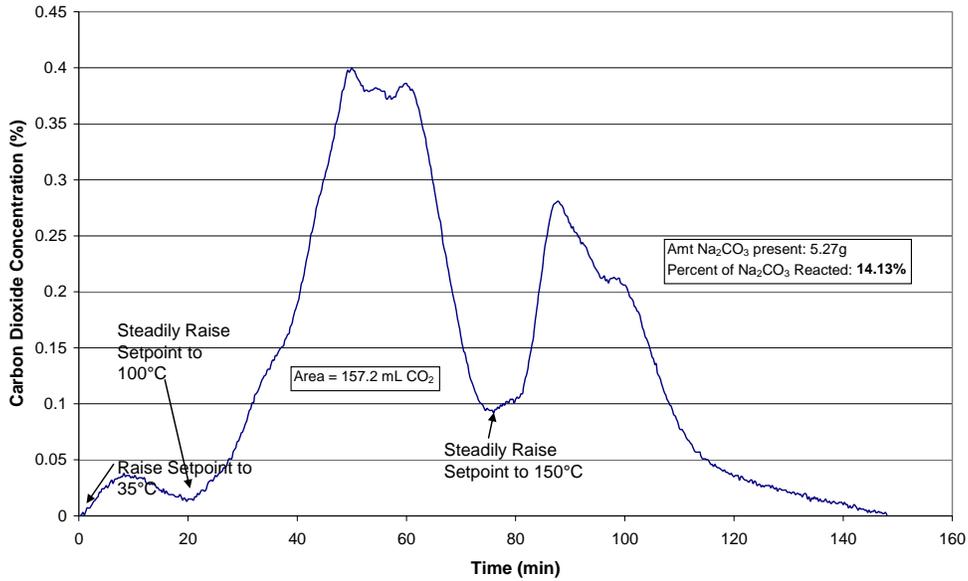


Figure 6. Sorbent SCI-110504-2 : Regeneration Cycle #2

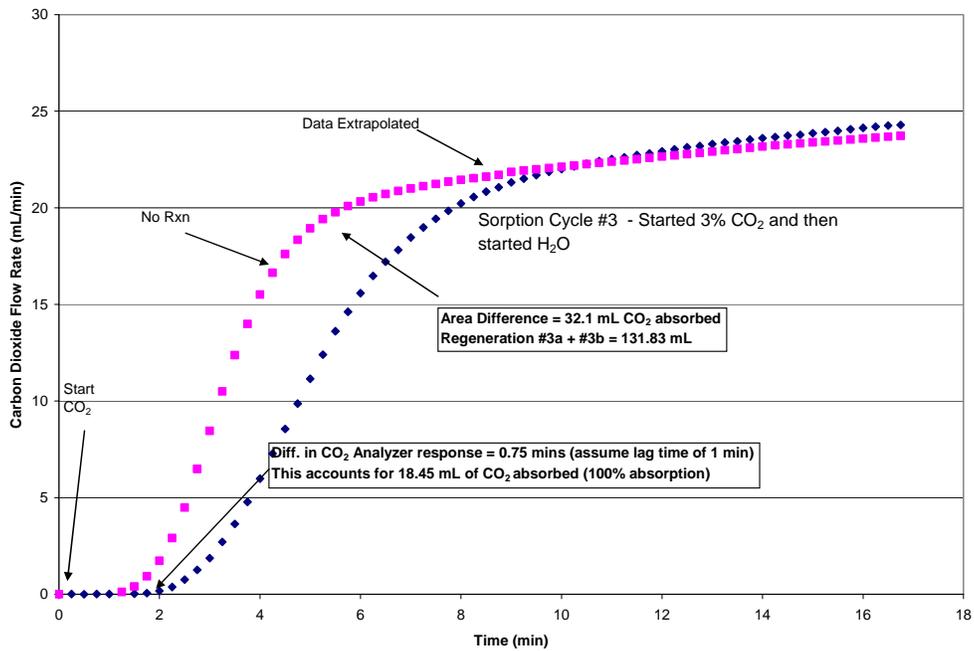
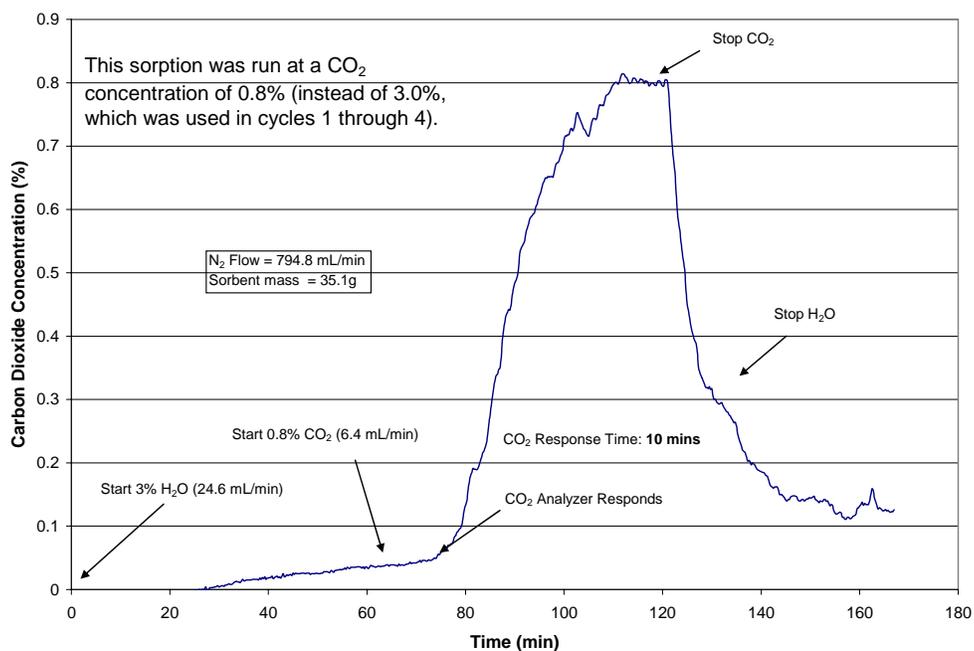
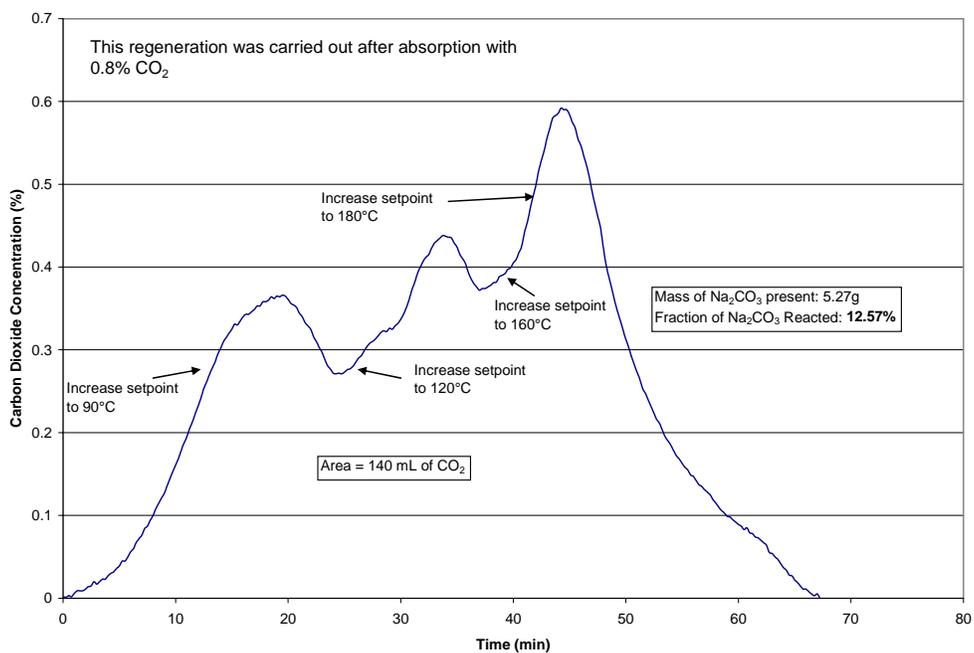


Figure 7. Sorbent SCI 110504-2 : Sorption Cycle #3



**Figure 8. Sorbent SCI-110504-2 : Sorption Cycle #5**



**Figure 9. Sorbent SCI-110504-2 : Regeneration Cycle #5**

The carbon dioxide recovered from the fifth regeneration was comparable to that of the earlier regenerations following sorption in a 3.0% carbon dioxide atmosphere. A summary of test results is given in Table 1.

**Table 1. Five Cycle Test of SCI-110504-2 - 15% Sodium Carbonate Sorbent**

	<b>Sorption #1 &amp; Regeneration #1</b>	<b>Sorption #2 &amp; Regeneration #2</b>	<b>Sorption #3 &amp; Regeneration #3a &amp; #3b</b>	<b>Sorption #4 &amp; Regeneration #4</b>	<b>Sorption #5 &amp; Regeneration #5</b>
Sorption Atmosphere	3% CO <sub>2</sub> then H <sub>2</sub> O	Start H <sub>2</sub> O 1st then 3% CO <sub>2</sub>	3% CO <sub>2</sub> then H <sub>2</sub> O	3% CO <sub>2</sub> then H <sub>2</sub> O	0.8% CO <sub>2</sub> then H <sub>2</sub> O
Sorption Temperature (°C)	60	60	60	60	60
Regeneration Atmosphere	nitrogen	nitrogen	Nitrogen	nitrogen	nitrogen
Regeneration Temp (°C)	150	150	150, 180	150	180
Amount CO <sub>2</sub> absorbed Total	140 mL	157 mL	131 mL	86 mL	140 mL
Fraction of Na <sub>2</sub> CO <sub>3</sub> Reacted	12.60%	14.10%	11.80%	7.75%	12.60%
CO <sub>2</sub> Response Time (min)	1.5	2.75	2.0	2.0	10.0
Amount CO <sub>2</sub> absorbed during 100% Absorp.	6.15 mL	36.9 mL	18.5 mL	18.5 mL	55.9 mL
Amount CO <sub>2</sub> absorbed after breakthrough	134 mL	120 mL	113 mL	67.8 mL	83.9 mL
Amount CO <sub>2</sub> absorbed according to comparison	~ same as #3	132 mL	32.1 mL	~ same as #3	not available

#### 4.1.2 Testing of SCI-111704-1

A second sorbent (SCI-111704-1) composed of 15% Na<sub>2</sub>CO<sub>3</sub> on an inert support was subjected to a single cycle of sorption and regeneration in the quartz reactor system. The reactor was loaded with 35.1 g of sorbent leading to an unexpanded bed depth of 3 in, and a height to diameter ratio of approximately 3. The sorption took place in an atmosphere of 0.8% carbon dioxide, 3.0% water vapor (balance nitrogen) at 60±2°C. Regeneration took place in nitrogen.

Sorption and regeneration data are shown in Figures 10 and 11. This material performed very similarly to the other SCI sorbent (SCI-110504-2). The overall capacity of the sorbent was 140 mL of carbon dioxide, which represented 12.6% of the sorbent (calculated to a sodium bicarbonate endpoint).

## 4.2 Properties of Supported Materials

This quarter two materials were prepared by a commercial catalyst manufacturer; fluidized bed testing of these materials was described in Section 4.1. In addition 5 supported sodium carbonate sorbents were prepared at RTI this quarter. Four of these materials were prepared by spray drying and one material was prepared an alternate method. The compositions and selected properties of these materials are shown in Table 2. This table also includes the properties of calcined SBC#3 and those of a support material, without incorporation of  $\text{Na}_2\text{CO}_3$ . Thermogravimetric analyzer (TGA) weight gains based on a 20-minute exposure to an atmosphere of 7.5% carbon dioxide and 5.9% water vapor at 60°C were used to compare carbonation activity of the different sorbents. Data from testing of two previously reported (Green, et al., 2004) materials was completed this quarter and are included in the Table.

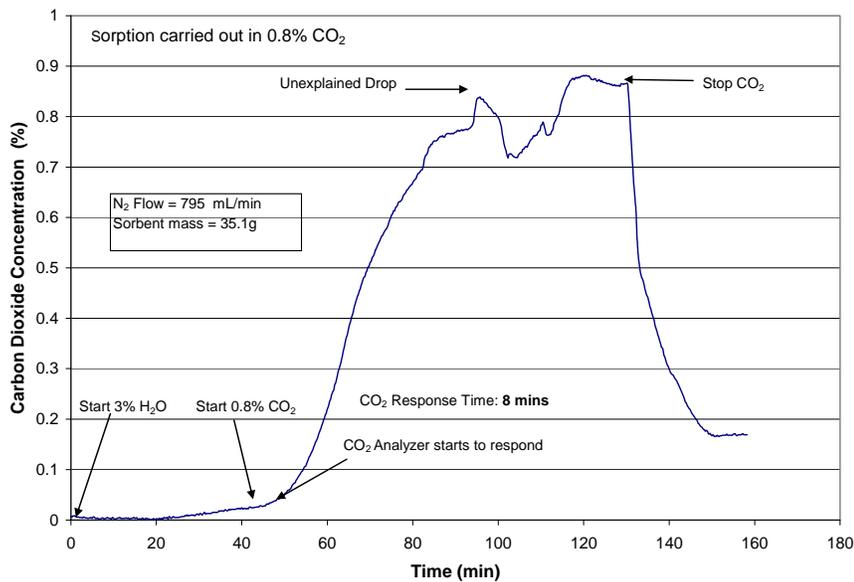


Figure 10. Sorbent SCI-111704-1 : Sorption Test

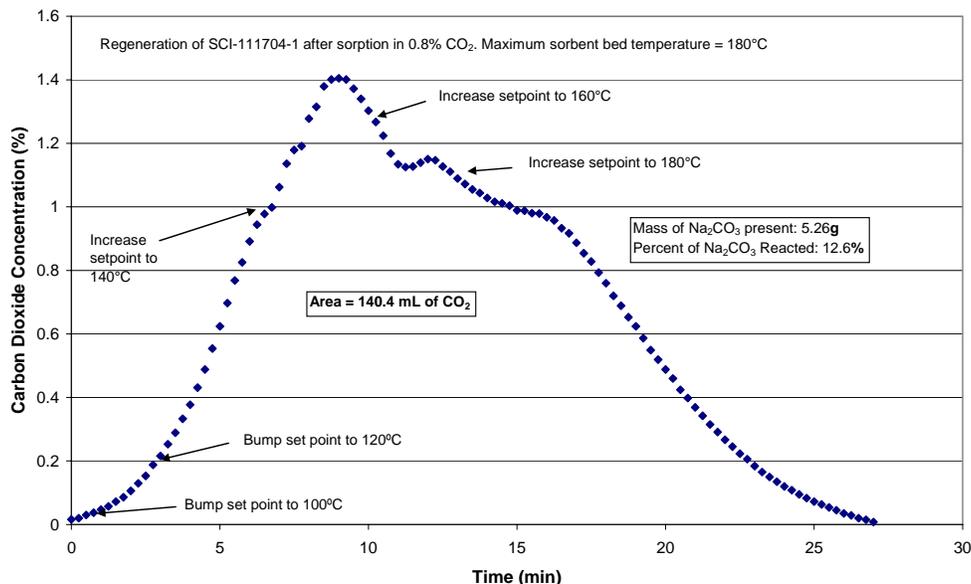


Figure 11. Sorbent SCI-111704-1 : Regeneration

Table 2. Supported Sorbent Characterization

Sample No.	Sodium Carbonate Content (%)	Compact Bulk Density g/mL	BET Surface Area (m <sup>2</sup> /g)	TGA Weight Gain—2-minutes (%)	Attrition Ratio
050704-1a	40	0.54	14.3	8.8	2.3
050704-3a	40	0.54	11.4	13.3	1.3
100804-2c	20	0.65	41.3	7.4	N/A
102104-2c	40	1.34	1.7	3.1	<1
102704-2c	40	0.68	10.6	8.1	N/A
110204-2c	40	10.6	0.09	3.6	N/A
110604-1c*	6.7	0.98	127	5.4	N/A
Calcined SBC-3	100	0.99	2.41	10.	N/A
FCC Catalyst	0	0.96	N/A	N/A	1.0

\*prepared by an alternate method  
N/A = not available

### 4.3 Mercury Adsorption Testing

Three different sorbent formulations were tested in the small scale screening apparatus: 20% sodium carbonate on alumina, 40% sodium carbonate on alumina, and 20% sodium carbonate on a silica-containing support. There was no detectable mercury collection by the alumina supported materials. The silica-containing material did show a small capture efficiency (approximately 10% of the mercury in the challenge gas).

This work indicates that mercury will not be trapped in the most likely candidate carbon dioxide sorbent formulations. Thus, disposal of spent sorbent will not be complicated by the presence of mercury. In terms of developing a multi-pollutant sorbent material, the modest activity of the silica-containing sample suggests a possible research lead.

#### 4.4 Transport Reactor Pilot Plant Test Plan Development

RTI has developed a preliminary test plan for pilot tests of the dry regenerable sorbent process to be conducted in the CANMET Energy Technology Centre “Mini-CFBC” unit. This reactor system consists of a heating section, a riser (10 cm I.D. by 5 m long), a cyclone, and a return leg. Solids can be continuously recirculated. The unit can be alternately operated as an entrained-bed absorber and as an entrained-bed regenerator. Inlet and outlet gas streams will be analyzed for change in CO<sub>2</sub> concentration.

Test conditions, subject to modification, are given in Table 3. The supported sorbent described above, will be tested and compared to pure sodium bicarbonate (SBC #3).

**Table 3. Pilot Scale Transport Reactor Test Conditions**

	<b>Sorption Mode</b>	<b>Regeneration Mode</b>
Riser Velocity (cm/sec)	450	450
Pressure (atm)	~1	~1
Temperature (°C)	40-65	120
Gas Flow Rate (slpm)	500	500
CO <sub>2</sub> content (%)	8	50
H <sub>2</sub> O content (%)	saturated	50
Nitrogen content	balance	0
Solids loading (g/L)	0.8-4.0	0.8-4.0
Circulation Rate (kg/hr)	25-250	25-250

#### 4.5 Other Project Activities

A topical report describing fluidized bed and fixed bed reactor testing, selected TGA screening and sorbent preparation work was submitted during the preceding quarter.

### 5.0 CONCLUSIONS

Fluidized bed testing of a supported material prepared at a commercial catalyst manufacturing facility showed relatively consistent carbon dioxide capacity over 5 cycles of sorption and regeneration. This material was composed of 15% sodium carbonate on an inert support. A similar material prepared by a less complicated method showed similar activity in a single cycle test.

A batch of approximately 20 kg of this supported sorbent was prepared, completing the milestone for 1Q FY05.

Lab scale spray dried batches of supported sorbents have been prepared at RTI. Some of these materials have much higher surface areas and greater attrition resistance than calcined sodium bicarbonate.

Promising regenerable carbon dioxide sorbents appear to adsorb only minimal quantities of mercury vapor under the expected conditions.

## **6.0 FUTURE WORK**

A test plan will be finalized and pilot-scale entrained-bed transport reactor testing of calcined SBC#3 and a large batch supported sorbent prepared according to the recipe of SCI 110504-2 will be conducted 2<sup>nd</sup> Quarter FY 05 in a single-loop transport reactor test facility.

An abstract of work completed in the previous year will be submitted to the Fourth Annual Conference on Carbon Capture and Sequestration.

A meeting will be held with representatives of Church and Dwight to discuss their involvement in additional project activities.

## **7.0 REFERENCES**

Green, D.A., Turk, B.S., Portzer, J. W., Gupta, R. P., McMichael, W. J., Liang, Y., and Harrison, D.P. Carbon Dioxide Capture From Flue Gas Using Dry Regenerable Sorbents, Quarterly Technical Progress Report, Research Triangle Institute, January 2003.

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