CARBON DIOXIDE CAPTURE FROM FLUE GAS USING DRY REGENERABLE SORBENTS

QUARTERLY TECHNICAL PROGRESS REPORT

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1.0 EXECUTIVE SUMMARY

The objective of this project is to develop a simple, inexpensive process to separate CO₂ as an essentially pure stream from a fossil fuel combustion system using a regenerable, sodium-based sorbent. The sorbent being used in this project is sodium carbonate which is converted to sodium bicarbonate, "baking soda," through reaction with carbon dioxide and water vapor. Sodium bicarbonate is regenerated to sodium carbonate when heated, producing a nearly pure CO₂ stream after condensation of water vapor.

Testing conducted previously confirmed that the reaction rate and achievable CO₂ capacity of sodium carbonate decreased with increasing temperature, and that the global rate of reaction of sodium carbonate to sodium bicarbonate increased with an increase in both CO₂ and H₂O concentrations. Energy balance calculations indicated that the rate of heat removal from the particle surface may determine the reaction rate for a particular particle system.

This quarter, thermogravimetric analyses (TGA) were conducted which indicated that calcination of sodium bicarbonate at temperatures as high as 200°C did not cause a significant decrease in activity in subsequent carbonation testing. When sodium bicarbonate was subjected to a five cycle calcination/carbonation test, activity declined slightly over the first two cycles but was constant thereafter. TGA tests were also conducted with two other potential sorbents. Potassium carbonate was found to be less active than sodium carbonate, at conditions of interest in preliminary TGA tests. Sodium carbonate monohydrate showed negligible activity.

Testing was also conducted in a 2-inch internal diameter quartz fluidized-bed reactor system. A five cycle test demonstrated that initial removals of 10 to 15 percent of the carbon dioxide in a simulated flue gas could be achieved. The carbonation reaction proceeded at temperatures as low as 41°C.

Future work by TGA and in fixed-bed, fluidized-bed, and transport reactor systems is planned to demonstrate the feasibility of this process in large scale operations to separate carbon dioxide from flue gas.

2.0 INTRODUCTION

Fossil fuels used for power generation, transportation, and by industry are the primary source of anthropogenic CO₂ emissions to the atmosphere. Much of the CO₂ emission reduction effort will focus on large point sources, with fossil fuel fired power plants being a prime target. The CO₂ 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 CO₂ 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 sodium-based sorbent to remove CO₂ from flue gases. Sorbent regeneration produces a gas stream containing only CO₂ and H₂O. The H₂O may be separated by condensation to produce a pure CO₂ stream for subsequent use or sequestration. The relevant reactions based upon the use of sodium bicarbonate as the sorbent precursor are:

and

Reaction (1) releases CO_2 and regenerates the sorbent, while Reaction (2) is used to capture CO_2 .

This report describes activities conducted between July 1, 2001 and September 30, 2001 by RTI and subcontractors Louisiana State University (LSU) and Church and Dwight (C&D). Activities conducted this quarter include electrobalance (thermogravimetric analysis [TGA]) studies at LSU and RTI, and fluidized-bed reactor testing at RTI.

3.0 EXPERIMENTAL

3.1 Electrobalance (Thermogravimetric Analysis) Testing at LSU

3.1.1 Sorbent Precursors

Six candidate Na-based sorbents have been studied—four grades of NaHCO_3 from C&D and two grades of trona (natural sodium sesquicarbonate, $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$) from Solvay. Selected properties of these materials, both as-received and following calcination, were reported in previous quarterly reports (Green et al., 2001a;b).

The following reactions of trona are slightly different from the direct reversible reaction of NaHCO_3 (Eq. 1). Trona is initially calcined according to

Subsequent carbonation and calcination reactions proceed according to

3.1.2 Previous Experimental Results

A summary of experimental results reported in the previous quarterly reports is presented below to provide background for the new results reported in this report. Although all samples were screened initially for reactivity, most of the earlier runs used sodium bicarbonate grade #3 (SBC#3), and the following summary pertains primarily to that material.

- Both the initial reaction rate and achievable CO_2 capacity decrease with increasing carbonation temperature, as expected from chemical equilibrium considerations.
- The possible formation of by-products including $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$, $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$, and $\text{Na}_2\text{CO}_3 \cdot 3\text{NaHCO}_3$ at carbonation conditions of interest was proven by thermodynamic analysis.
- At constant temperature, the global reaction rate increases with an increase in both CO_2 and H_2O concentrations.

- The shape of the sample pan, quartz cup versus flat aluminum pan, had relatively little effect on the global rate during TGA tests.
- The global reaction rate was influenced by the volumetric flow rate of carbonation gas in the TGA. As a result the 300 scc/min flow rate used in most of the early tests has been replaced by a carbonation gas flow rate of 600 scc/min.

3.1.3 Experimental Conditions

Base case reaction conditions for TGA tests at LSU are shown in Table 1. Results from experimental tests to examine the effect of carbonation and calcination temperature and gas composition are compared to results from these base case conditions. Base case carbonation gas composition approximates the flue gas composition resulting from the combustion of natural gas using 10% excess air. Base case calcination conditions (which may not be practical in commercial operation), were selected to minimize sorbent activity loss during regeneration.

Table 1. Base Reaction Conditions

Calcination	Temperature	120 °C
	Pressure	1 atm
	Gas Composition	100% He
Carbonation	Temperature	70 °C
	Pressure	1 atm
	Gas Composition	8 mol% CO ₂ 16 mol% H ₂ O 76 mol% He
	Gas Flow Rate	600 scc/min

The following experimental procedure is used in base case tests. An initial charge of approximately 70 mg of sorbent precursor is heated from room temperature to 100 °C at a rate of 5 °C/min and from 100 °C to the final calcination temperature of 120 °C at a rate of 1 °C/min under flowing He. After calcination is complete (as indicated by constant weight), the temperature is decreased at a rate of 2 °C/min still under He to the 70 °C carbonation temperature. The gas composition is then changed to 8 mol% CO₂, 16 mol% H₂O, balance He flowing at 600 scc/min and carbonation is continued until the reaction rate approaches zero as indicated by constant weight. Appropriate changes in this procedure are made when carbonation and calcination temperatures and gas compositions are altered from the base case. Reaction conditions for all tests completed this quarter are summarized in Tables 2a and 2b.

3.2 Thermogravimetric Analysis at RTI

RTI conducted additional thermogravimetric analyses this quarter using the apparatus and procedure described in Green et al. (2001a). Two new materials were subjected to preliminary testing for characterization and to investigate their suitability for use as sorbents. Potassium carbonate, extra fine, anhydrous (specification sheet included as Appendix A) was obtained from Armand Products Company, and exposed to simulated flue gas at 60 and 70 °C. This material was tested for comparison to sodium carbonate and to determine if it was a feasible sorbent at conditions of interest. Sodium carbonate monohydrate was obtained from C&D, and exposed to simulated flue gas at 60, 70 and 80 °C. This material was tested to determine if the water incorporated in its structure would improve the rate of reaction.

Table 2a. TGA Reaction Conditions Used in Experimental Tests Completed with Trona (T-50) This Quarter

Run No.	Initial Weight mg	Calcination Conditions				Carbonation Conditions				
		Temp. °C	Gas Composition		Flow scc/min	Temp. °C	Gas Composition			Flow scc/min
			He	CO ₂			CO ₂	H ₂ O	He	
59	69.7	120	100	0	186	70	8	16	76	300
60	71.8	120	100	0	186	70	8	16	76	300
61	71.2	120	100	0	186	60	8	16	76	300
62	71.4	120	100	0	186	80	8	16	76	300
63	71.3	120	100	0	186	60	8	16	76	300
64	71.2	120	100	0	414	70	8	16	76	600
65	70.2	120	100	0	414	80	8	16	76	600
66	70.0	120	100	0	414	60	8	16	76	600
67	65.6	120	100	0	450	70	8	10	82	600
68	70.1	120	100	0	480	70	8	5	87	600
69	69.4	120	100	0	450	70	8	10	82	600
70	67.6	120	100	0	450	70	8	10	82	600
71	65.3	120	100	0	402	70	10	16	74	600
72	67.6	120	100	0	402	70	10	16	74	600
73	69.0	120	100	0	432	70	5	16	79	600
74	70.1	120	100	0	432	60	5	16	79	600
75	64.5	120	100	0	432	80	5	16	79	600
76	68.5	200	0	100	200	No carbonation				
77	75.2	120	100	0	414	80	8	16	76	600
78	76.3	120	100	0	414	80	8	16	76	600
79	73.6	120	100	0	414	80	8	16	76	600

Table 2b. TGA Reaction Conditions Used in Experimental Tests Completed with SBC#3 Sorbent^a This Quarter

Run No.	Initial Weight mg	Calcination Conditions					Carbonation Conditions				
		Temp. °C	Gas Composition			Flow scc/min	Temp. °C	Gas Composition			Flow scc/min
			He	CO ₂	H ₂ O			CO ₂	H ₂ O	He	
80	70.5	170	0	100	0	200	70	8	16	76	600
81	73.9	150	0	100	0	200	70	8	16	76	600
82	74.3	150	0	100	0	200	60	8	16	76	600
83	73.0	120	100	0	0	414	70	8	16	76	600
84	72.9	200	0	100	0	200	70	8	16	76	600
85	70.2	120	0	100	0	200	70	8	16	76	600
86	72.6	120	100	0	0	414	70	8	16	76	600
87	74.5	120	100	0	0	414	70	8	16	76	600
88	72.0	120	100	0	0	414	70	8	16	76	600
89	71.2	150	0	80	20	250	70	8	16	76	600
90	72.0	200	0	80	20	250	70	8	16	76	600
91	76.0	120	100	0	0	414	70	8	16	76	600

^aCarbonation gas was composed of 8% CO₂, 16% H₂O, and 76% He.

3.3 Fluidized-Bed Reactor Testing at RTI

RTI conducted a five cycle calcination/carbonation test using SBC#3 in a 2-inch internal diameter fluidized bed reactor system. The reactor and associated instrumentation is shown in Figure 1.

Figure 1. Fluidized-bed test reactor system.

In the testing conducted this quarter, three electronic mass flow controllers (MFC) were used to meter nitrogen, air, and carbon dioxide from compressed gas cylinders. These MFC were calibrated against a soap bubble flow meter. Deionized water was added to the mixed dry gas stream using a high pressure liquid chromatography (HPLC) pump. The reactor consisted of a 2-inch internal diameter quartz tube, fitted with a 3-mm thick porous quartz plate distributor. The reactor was suspended within a flanged 4-inch stainless steel pipe that was surrounded by a three zone electric furnace. Inlet gas entered the top flange of the pipe, passed through the annulus, and entered the quartz reactor through the distributor at the bottom. A 6-inch bed of SBC#3 was initially charged to the reactor to maintain a length to diameter ratio of 3. Effluent gas passed through a shell and tube heat exchanger for condensation of steam, a Hartmann and Braun Model URAS-14 nondispersive infrared carbon dioxide monitor and an oxygen sensor. The sorbent bed contained 3 Type-K-thermocouples spaced at 1, 3, and 5 inches above the distributor. An electronic differential pressure gauge connected with a digital display indicated the pressure drop across the bed. Total pressure was also monitored.

Information about the process is collected and recorded by the "Lab View" package, an advanced data acquisition software/hardware package from National Instruments. The software has been programmed to facilitate the monitoring of the process providing bed temperatures, inlet gas temperature, reactor pressure, pressure drop, inlet gas flow rates, and outlet carbon dioxide and oxygen concentrations.

4.0 RESULTS AND DISCUSSION

4.1 Electrobalance Testing at LSU

Most of the tests reported in the previous quarterly report used SBC#3. Trona T-50 was used in early tests during the present quarter. However, as shown below, reproducibility in tests using this sorbent is not as good as in tests with the SBC materials. SBC#3 was used in the later tests, and reproducibility was considerably better.

Standard calcination conditions were used in all Trona T-50 tests, and the effects of carbonation temperature and gas composition were studied. Standard carbonation conditions were used with the SBC#3 sorbent, and the effects of calcination temperature and gas composition were examined by comparing the carbonation kinetics in the subsequent carbonation cycle. Calcination temperature was varied from 120 to 200°C and calcination was carried out using both pure CO₂ and a mixture of 80% CO₂ and 20% H₂O. These compositions are more representative of calcination atmospheres expected in a commercial process. In addition, the first multicycle test TGA consisting of five complete calcination and carbonation cycles was completed using SBC#3.

4.1.1 Trona T-50 Results

4.1.1.1 Reaction Reproducibility and the Effect of Carbonation Temperature. Dimensionless weight-time results for Tests 59 through 63 are shown in Figure 2. These results show the effect of carbonation temperature (60, 70, and 80°C) as well as reaction reproducibility at 60°C (Tests 61 and 63) and 70°C (Tests 59 and 60). Standard calcination conditions were used, and the carbonation gas contained 8% CO₂, 16% H₂O, and balance He at a total flow rate of 300 scc/min. Initial dimensionless weights were all quite close to the theoretical value of 0.723 for T-50 indicating that complete calcination was always obtained.

Figure 2. Dimensionless weight-time results for T-50 showing reaction reproducibility and the effect of carbonation temperature at a flow rate of 300 scc/min.

Both sets of duplicated tests show excellent reproducibility. The initial reaction rate is highest at 80°C, somewhat lower at 70°C, and a minimum at 60°C. This is counter to results for SBC#3 reported in the previous quarterly report where the initial rate decreased with increasing temperature. The initial rate reported for T-50 from earlier screening tests was a maximum at 60°C, intermediate at 80°C, and a minimum value at 70°C. The maximum final dimensionless weight occurred at 60°C, with both 70°C and 80°C results showing approximately the same final value. SBC#3 tests reported earlier showed that the final dimensionless weight decreased with increasing temperature.

If it is assumed that NaHCO_3 is the only product of carbonation, the final dimensionless weight of 0.92 at 70°C and 80°C corresponds to about 50% carbonation, while the final value of 0.98 at 60°C corresponds to about 65% carbonation. However, results of thermodynamic analysis reported previously show the possibility of by-product formation at all test temperatures using this gas composition. These final percent carbonation values are in reasonable agreement with results from the earlier screening tests, which showed between 45 and 50% carbonation at 80°C, just above 50% carbonation at 70°C, and 67% carbonation at 60°C.

The effect of carbonation temperature at a higher flow rate of 600 scc/min is shown in the dimensionless weight-time curves of Figure 3. The gas composition and temperatures were the same as discussed above. In this case the initial rate was in the order of 70°C > 80°C > 60°C, while final dimensionless weights varied between 0.92 and 0.94, which corresponds to final fractional carbonations between 50 and 55%.

The order of the initial rates is quite different from that observed at 300 scc/min (Figure 2) and the final fractional carbonation at 60°C is considerably lower than observed from the 300 scc/min data. Final fractional conversions at both 70°C and 80°C are about equal to those

Figure 3. Dimensionless weight-time results for T-50 showing the effect of carbonation temperature at a flow rate of 600 scc/min.

observed at 300 scc/min. These unexpected results provide examples of the lack of reproducibility with the T-50 samples.

Results of additional reproducibility tests are shown in Figure 4. Carbonation flow rate and temperature were 600 scc/min and 70 °C, respectively, but the H₂O content of the carbonation gas was reduced to 10% (replaced by He). Results from two tests (67 and 70) were effectively identical, but both the initial and final dimensionless rates were significantly larger in Test 69.

The final dimensionless weights in Tests 67 and 70 corresponded to about 48% carbonation while the final carbonation in Test 69 was about 50%. A reduction in initial rate associated with the reduced H₂O content is not unexpected. However, the increase in the final fractional carbonation was unexpected. This value should be independent of H₂O, as long as there is sufficient H₂O present to make the reaction thermodynamically favored.

4.1.1.2 Effect of Carbonation Gas Composition. The effect of CO₂ concentration is shown in Figure 5. Standard conditions were used in Test 64 while the CO₂ content was increased to 10% in Test 71 and reduced to 5% in Test 73. The initial rates were approximately equal at 8% and 10% CO₂ and were considerably larger than the initial rate at 5% CO₂. However, the final dimensionless weight using 5% CO₂ was significantly larger and corresponded to about 65% carbonation, while the final carbonations using 8% and 10% CO₂ were about 50% and 45%, respectively.

The most obvious difference in the results indicated by Figure 5 is that, in spite of the lower initial rate observed with 5% CO₂, the reaction continued to occur for a much longer time. Dimensionless weights from all three tests were equal after about 80 min, and the reaction was still occurring slowly after 150 min in 5% CO₂. Similar results in other gas-solid noncatalytic reactions have been explained on the basis of higher reaction rates associated with higher CO₂ concentrations causing more rapid pore closure. Smaller reaction rates at lower CO₂

Figure 4. Dimensionless weight-time results for T-50 showing reaction reproducibility at a flow rate of 600 scc/min.

Figure 5. Dimensionless weight-time results for T-50 showing the effect of CO₂ concentration.

concentration distributes the reaction in a broader zone within the sorbent particle, and postpones, or even avoids pore closure.

The effect of H₂O content was examined in Tests 64 (16% H₂O), 67 (10% H₂O), and 68 (5% H₂O), and results are compared in Figure 6. Other carbonation conditions were indicated in Table 1. The initial rate increased with increasing H₂O, while the final dimensionless weight was approximately equal in 5% and 10% H₂O, and somewhat larger in 16% H₂O.

Figure 6. Dimensionless weight-time results for T-50 showing the effect of H₂O concentration.

4.1.1.3 Reproducibility After Sieving. As illustrated above, carbonation results using T-50 sorbent were not as reproducible as desired. All previous tests had used randomly acquired samples of as-received sorbent precursor. Variations in composition because of impurities and/or particle size were considered to be possible causes of the problem. While impurity variations could not be eliminated, the possible effect of variable particle size was eliminated by sieving the as-received sorbent and selecting the 60-70 mesh size range for testing.

Three duplicate tests (77, 78, and 79) using standard carbonation conditions were carried out using sieved material. Results are shown in Figure 7 along with results from Test 65, also at standard reaction conditions, but using as-received T-50. Once again, there is a considerable range in initial rates with the as-received unsieved material showing the highest initial rate, Tests 78 and 79 showing approximately the same (intermediate) rate, and Test 77 producing a significantly lower initial rate. Final dimensionless weights were all approximately equal and ranged only from 0.91 to 0.92, corresponding to 48% to 50% carbonation. These results indicate that particle size variations were not the cause of the reproducibility problems.

Figure 7. Reproducibility of T-50 carbonation results using sieved samples.

4.1.2 SBC Grade #3 Results

4.1.2.1 Reproducibility. Even though earlier tests showed adequate reproducibility using SBC#3, reproducibility problems using Trona T-50 were a cause of concern. Consequently, Tests 86, 87, and 88 were conducted at standard reaction conditions to re-establish the fact that reproducible results could be obtained using SBC#3. Results are shown in Figure 8. While there is some variation in initial rates, the overall results are quite reproducible, and all final dimensionless weights are effectively equal to 0.84, which corresponds to about 57% carbonation. In addition, these final dimensionless weights correspond closely to comparable values reported previously.

4.1.2.2 The Effect of Calcination Temperature In a Pure CO₂ Atmosphere. As previously stated, standard calcination conditions of 120°C in He were chosen to minimize the severity of sorbent exposure. In reality, however, calcination would occur in an atmosphere having a high CO₂ content and perhaps at a temperature substantially higher than 120°C. A series of tests using a pure CO₂ calcination atmosphere and with the calcination temperature ranging from 120°C to 200°C was carried out. Calcination at 120°C in pure CO₂ is probably impractical because of the very slow calcination rate; results from this test, however, provide a direct evaluation of the effect of calcination atmosphere. The effect of calcination conditions was then observed by comparing the results from the subsequent carbonation cycle using standard carbonation conditions.

Carbonation results following calcination in pure CO₂ at four temperatures are compared in Figure 9 with carbonation results following calcination under standard conditions of 120°C in He. There is essentially no difference in the initial reaction rates. The dimensionless weight-time curves are almost identical for the first 50 mins. Thereafter there is a small spread in the results, but the final dimensionless weights vary only between 0.83 and 0.86, corresponding to

Figure 8. Reproducibility of SBC#3 carbonation results using standard reaction conditions.

Figure 9. The effect of calcination temperature in pure CO₂.

final carbonations between 54 and 62%. Thus it is clear that calcination at a temperature as high as 200°C in pure CO₂ has little, if any, negative effect on first cycle carbonation performance.

4.1.2.3 The Effect of Calcination Temperature in a CO₂/H₂O Atmosphere. Process simulation results reported in the previous quarterly report (Green et al., 2001c) were based on a calcination atmosphere containing 80% CO₂ and 20% H₂O. Consequently, tests using this calcination atmosphere were carried out at temperatures of 150°C and 200°C. Results of the subsequent carbonation cycle are compared to results using standard calcination conditions of 120°C in He in Figure 10. Once again, results from all three runs are quite close. If anything, the two carbonation tests following higher temperature calcination in CO₂/H₂O produced slightly higher final dimensionless weights. Clearly, the higher temperature calcination in the CO₂/H₂O atmosphere had little effect on first cycle carbonation performance.

Figure 10. The effect of calcination temperature in 80% CO₂/20% H₂O.

4.1.2.4 Five-Cycle Results. In order for this CO₂ capture concept to be economically viable, it will be necessary that the sorbent be durable and maintain carbonation activity through many calcination-carbonation cycles. Preliminary information on sorbent durability was obtained in five-cycle Test 91.

Standard calcination and carbonation conditions were used in each cycle. Dimensionless weight-time results for each carbonation cycle are shown in Figure 11. Results, both in terms of initial rate and final dimensionless weight, were most favorable in Cycle 1, with a clear decrease in both values between Cycle 1 and Cycle 2. The final Cycle 1 dimensionless weight of 0.87, corresponding to 65% carbonation, was in reasonable agreement with previous single cycle result. The final dimensionless weight decreased to 0.82 in Cycle 2 (51% carbonation). However, the final dimensionless weights in cycles 3, 4, and 5 were all about 0.80, corresponding to 46% carbonation.

Figure 11. Five-cycle carbonation results using standard reaction conditions.

4.2 Thermogravimetric Testing at RTI

4.2.1 Testing of Potassium Carbonate

Potassium carbonate (extra fine, anhydrous) was subjected to preliminary testing at 60 and 70°C, for comparison to calcined sodium bicarbonate. Data from tests conducted with 5.8% H₂O and 7.5% CO₂ are shown in Figures 12 and 13.

At both temperatures the material reacted rapidly upon initial exposure to simulated flue gas. Based on a theoretical weight gain of 45% (based on complete conversion to potassium bicarbonate), the reaction rate was slower than that observed in tests with sodium bicarbonate. After two hours exposure to the simulated flow gas, the atmosphere was switched back to dry helium. At 70°C the material began to slowly lose weight. This weight loss did not occur at 60°C. This observation could be explained if the weight gain at 70°C was not because of formation of potassium bicarbonate but rather to hydrate formation. Alternately, potassium bicarbonate may be unstable at 70°C in a carbon dioxide free atmosphere and revert to potassium carbonate.

4.2.2 Testing of Sodium Carbonate Monohydrate

Sodium carbonate monohydrate was subjected to preliminary testing at 60, 70, and 80°C, for comparison to calcined sodium bicarbonate. Data from tests conducted with 5.8% H₂O and 7.5% CO₂ are shown in Figures 14, 15, and 16.

Figure 12. TGA of potassium carbonate (60°C).

Figure 13. TGA of potassium carbonate (70°C).

Figure 14. TGA of sodium carbonate monohydrate (60°C).

Figure 15. TGA of sodium carbonate monohydrate (70°C).

Figure 16. TGA of sodium carbonate monohydrate.

Under the test conditions, the activity of this material was minimal at 60 and 70°C suggesting that this form of sodium carbonate would not be useful as a sorbent for CO₂. At 80°C it slowly changes to the unhydrated form, even in the presence of 5.8% steam. This change occurs rapidly starting at a temperature somewhere above 80°C.

4.3 Fluid-Bed Reactor Testing at RTI

A five cycle calcination/carbonation test was conducted in a fluidized bed reactor. Temperatures for the carbonation cycles varied from cycle to cycle, as the range of feasible operating temperatures was determined. While the reactor was preheated prior to carbonation, the exothermic heat of reaction ultimately controlled the reaction temperature, and no additional heat input, beyond the influent gas preheater, was necessary to maintain the bed temperature. Slight variations in temperature across the fluidized sorbent bed occurred. The reactor was initially loaded with 258 g of SBC#3, providing an initial bed height of 6-inches, for a height to diameter ratio of 3. The material was calcined *in-situ* prior to the first carbonation and between subsequent carbonations. Calcinations were essentially complete, based on, in some cases, the carbon dioxide content of the reactor effluent gas, and in all cases, monitored bed temperatures.

Carbon dioxide removal was calculated based on inlet flows (dry basis) of air, nitrogen and CO₂, and CO₂ content (dry basis) of the effluent gas. Carbon dioxide removal profiles for each cycle are shown in Figures 17 through 21. Cycle lengths varied from approximately 3 to 6.5 hours. Temperature profiles at 1-in, 3-in, and 5-in above the flow distributor are shown in Figures 22 through 26.

Figure 17. Cycle 1 carbonation test (9/19/01) - fractional CO₂ removal.

Figure 18. Cycle 2 carbonation test (9/20/01) - fractional CO₂ removal.

Figure 19. Cycle 3 carbonation test (9/25/01) - fractional CO₂ removal.

Figure 20. Cycle 4 carbonation test (9/26/01) - fractional CO₂ removal.

Figure 21. Cycle 5 carbonation test (9/27/01) - fractional CO₂ removal.

Figure 22. Temperature profile - Cycle 1 (9/19/01).

Figure 23. Temperature profile - Cycle 2 (9/20/01).

Figure 24. Temperature profile - Cycle 3 (9/25/01).

Figure 25. Temperature profile - Cycle 4 (9/26/01).

Figure 26. Temperature profile - Cycle 5 (9/27/01).

A summary of test results is given in Table 3. The temperature data in this table are based on the average temperature (for the three measurement locations) during the carbonation cycle, which varied as the exothermic effects of the reaction declined. The water vapor content of the reactant gas was limited in the lower temperature cycles to avoid supersaturation.

Based on these data there was no obvious decline in sorbent activity over five cycles in contaminant-free simulated flue gas. The sorbent was removed from the reactor after the fifth cycle. This material will be subjected to characterization tests, and compared to freshly calcined SBC#3. Slow reaction rates in the low reaction temperature range (where thermodynamic considerations become more favorable) do not appear to limit the range at which the carbonation reaction can be conducted.

Table 3. Summary of 5 Cycle Carbonation Test Data

Cycle	1	2	3	4	5
Total Flow (SLPM)	10.1	10.2	10.4	10.2	10.4
Dry Flow (SLPM)	8.5	8.7	9.2	9.6	10.0
CO ₂ in (dry %)	6.6	8.1	7.6	7.3	7.0
H ₂ O in (%)	16.0	16.5	11.9	6.1	4.5
Temperature (°F)	169	159	148	135	105
CO ₂ removed (g)	26.4	26.1	26.2	26.4	44.1
Sorbent Capacity Utilization (%)	39.1	38.6	38.8	39.1	65.2
Exposure Time (min)	210	260	175	175	390

4.4 Plans for Next Quarter

LSU will continue work to determine the reaction mechanisms of the carbonation reaction. RTI will conduct additional cyclic fluidized bed tests on sodium bicarbonate and trona. RTI and C&D will begin work related to design of a transport reactor system for the carbonation phase of the cycle. A meeting is planned in early December to review the project program.

5.0 CONCLUSIONS AND FUTURE WORK

Results of thermogravimetric analyses of trona were not as reproducible as desired. This was particularly true with respect to initial rate as indicated, for example, in Figures 4 and 7. Final percent carbonation, based on the assumption that NaHCO₃ is the only product formed, was generally in the range of 48 to 55%. In two tests having small initial rates, the carbonation reaction continued slowly and reached about 65% when the test was stopped after 150 minutes. Sieving the as-received T-50 and selecting the 60 to 70-mesh size range to eliminate the possible effect of variable particle size did not improve experimental reproducibility.

Satisfactory reproducibility was achieved in thermogravimetric analyses of SBC#3. Calcination in 100% CO₂ and in 80% CO₂/20% H₂O at temperatures as high as 200°C did not cause significant reduction in the activity in the subsequent carbonation cycle. An initial multicycle test consisting of five complete calcination-carbonation cycles at standard conditions showed some decrease in activity between Cycles 1 and 2 and also between Cycles 2 and 3. However, activity was effectively constant in Cycles 3, 4, and 5.

Thermogravimetric testing of potassium carbonate at 60°C suggested that it was less reactive than calcined sodium bicarbonate. At 70°C, the observed weight gain may have been because of hydrate formation, rather than formation of potassium bicarbonate.

Preliminary testing of sodium carbonate monohydrate suggested that this compound did not react significantly with simulated flue gas, and that there would be no advantage to attempting to regenerate sodium bicarbonate to this form for subsequent carbonation.

Initial CO₂ removals of 10 to 15% from simulated contaminant free flue gas were observed through five calcination/carbonation cycles in a fluidized bed reactor system with SBC#3 as the starting material. The carbonation reaction proceeded at temperatures as low as 41 °C. These findings are quite significant given the low temperature for carbonation reaction (limiting the kinetics) and very short residence time in a fluidized-bed. Based on these preliminary results, it may be possible to operate this process in a transport reactor. This evaluation will be performed in next quarter to determine the most cost-effective configuration for the process.

6.0 REFERENCES

Green, D.A., Turk, B.S., Gupta, R., and Lopez Ortiz, A., Carbon Dioxide Capture From Flue Gas Using Dry Regenerable Sorbents, Quarterly Technical Progress Report, Research Triangle Institute, January 2001(a).

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Appendix A

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**POTASSIUM CARBONATE
EXTRA FINE, ANHYDROUS**

SALES SPECIFICATION

Component	Basis	Specification ¹
Total Alkalinity (as K ₂ CO ₃)	wt. %	98.5 Min.
KOH	wt. %	0.20 Max.
KCl	wt. %	0.01 Max.
H ₂ O	wt. %	1.0 Max.
Na	wt. %	0.38 Max.
K ₂ SO ₄	ppm by wt.	75 Max.
As	ppm by wt.	3.0 Max.
Fe	ppm by wt.	2.0 Max.
Heavy Metals (as Pb)	ppm by wt.	5.0 Max.
Hg	ppm by wt.	0.05 Max.
Ni	ppm by wt.	1.0 Max.

Particle Size Distribution (not a specification item)

Typical Range

80% min. through 325 mesh

Notes:

¹ Meets Food Chemical Codex (FCC) and The United States Pharmacopeia/The National Formulary (USP/NF) specifications.

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