CARBON DIOXIDE CAPTURE FROM FLUE GAS USING DRY REGENERABLE SORBENTS

QUARTERLY TECHNICAL PROGRESS REPORT

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TABLE OF CONTENTS

Page

LIST OF FIGURES

LIST OF TABLES

1.0 EXECUTIVE SUMMARY

The objective of this project is to develop a simple and inexpensive process to separate 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 primarily alkali carbonates, and particularly sodium carbonate and potassium carbonate, which are converted to bicarbonates or intermediate salts through reaction with carbon dioxide and water vapor. Bicarbonates are regenerated to carbonates when heated, producing a nearly pure CO_2 stream after condensation of water vapor.
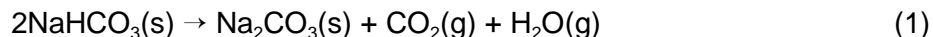
This quarter, electrobalance tests suggested that high calcination temperatures decrease the activity of sodium bicarbonate Grade 1 (SBC#1) during subsequent carbonation cycles, but there is little or no progressive decrease in activity in successive cycles. SBC#1 appears to be more active than SBC#3. As expected, the presence of SO_2 in simulated flue gas results in a progressive loss of sorbent capacity with increasing cycles. This is most likely due to an irreversible reaction to produce Na_2SO_3. This compound appears to be stable at calcination temperatures as high as 200°C.

Tests of 40% supported potassium carbonate sorbent and plain support material suggest that some of the activity observed in tests of the supported sorbent may be due to adsorption by the support material rather than to carbonation of the sorbent.

2.0 INTRODUCTION

Fossil fuels used for power generation, transportation, and by industry are the primary source of anthropogenic CO_2 emissions to the atmosphere. Much of the CO_2 emission reduction effort will focus on large point sources, with fossil fuel fired power plants being a prime target. The CO_2 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_2 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 to remove CO_2 from flue gases. Sorbent regeneration produces a gas stream containing only CO_2 and H_2O. The H_2O may be separated by condensation to produce a pure CO_2 stream for subsequent use or sequestration. The primary reactions, based upon the use of sodium bicarbonate (SBC) as the sorbent precursor and sodium carbonate as the reaction product are:

$$2NaHCO_3(s) \rightarrow Na_2CO_3(s) + CO_2(g) + H_2O(g) \quad\quad (1)$$

and

$$Na_2CO_3(s) + CO_2(g) + H_2O(g) \rightarrow 2NaHCO_3(s) \qu\quad (2)$$
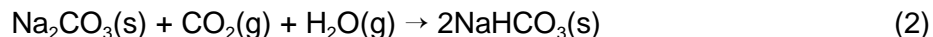
Reaction (1) releases CO_2 and regenerates the sorbent, while Reaction (2) is used to capture CO_2. Several other solid products, intermediate between sodium carbonate and sodium bicarbonate, may also be produced under the anticipated reaction conditions. An intermediate

1

compound, $Na_2CO_3 \cdot 3NaHCO_3$, known as Wegscheider's salt, forms at the reaction conditions of interest.

Analogous reactions (Reactions 3 and 4) take place within the potassium carbonate system:

$$2KHCO_3(s) \rightarrow K_2CO_3(s) + CO_2(g) + H_2O(g) \tag{3}$$

and

$$K_2CO_3(s) + CO_2(g) + H_2O(g) \rightarrow 2KHCO_3(s). \tag{4}$$

A compound salt of potassium carbonate and potassium bicarbonate is also thought to be of importance at the conditions of interest.

Trona (sodium sesquicarbonate) can also be used as a sorbent precursor. The following reactions of trona are slightly different from the direct reversible reaction of $NaHCO_3$ (reaction 1). Trona is initially calcined according to:

$$2[Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O(s)] \rightarrow 3Na_2CO_3(s) + CO_2(g) + 5H_2O(g) \tag{5}$$
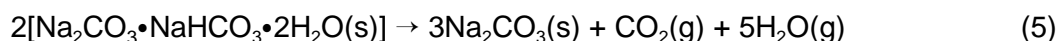
Subsequent carbonation and calcination reactions proceed according to:
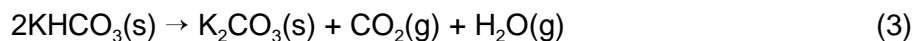
$$Na_2CO_3(s) + CO_2(g) + H_2O(g) \leftrightarrow 2NaHCO_3(s) \tag{6}$$
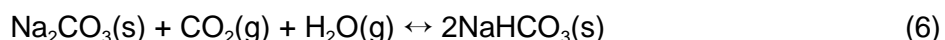
This report describes activities conducted between October 1, 2002 and December 31, 2002 by RTI and its subcontractors Louisiana State University (LSU) and Church and Dwight (C&D). Activities conducted this quarter include electrobalance (thermogravimetric analysis [TGA]) and fixed bed reactor studies at LSU and TGA and sorbent preparation activities at RTI. In addition, RTI continued development of mathematical models and modified a reactor system for studies with simulated flue gas containing the potentially corrosive contaminants (SO_2 and HCl).

3.0 EXPERIMENTAL

3.1 Electrobalance Testing at LSU

3.1.1 Sorbents Used

Thermogravimetric analysis (TGA) testing was conducted at LSU with trona Grade T-200, and SBC, Grades 1 and 3. Selected properties of these materials, and other sorbents used (both as-received and following calcination), were reported in previous quarterly reports (Green et al., 2001a; b).

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 early detailed testing used SBC#3. More recently

this study has been expanded to include SBC#1, Trona T-50 and Trona T-200. Because of somewhat different results, separate summaries are presented for SBC#3 and the trona samples.

3.1.2.1 SBC #3

1. Both the initial reaction rate and achievable CO_2 capacity decrease with increasing carbonation temperature.

2. The possible formation of by-products including $Na_2CO_3 \bullet H_2O$, $Na_2CO_3 \bullet NaHCO_3 \bullet 2H_2O$, and $Na_2CO_3 \bullet 3NaHCO_3$ (Wegscheider's salt) at carbonation conditions of potential interest was proven by thermodynamic analysis confirmed experimentally.

3. At constant temperature, the global carbonation reaction rate increases with an increase in both CO_2 and H_2O concentrations.

4. Calcination in 100% CO_2 and 80% CO_2/20% H_2O at temperatures as high as 200°C did not cause a significant reduction in the sorbent activity in the subsequent carbonation cycle.

5. Five-cycle tests using SBC#3 at standard carbonation and calcination conditions show a gradual loss in both reaction rate and final fractional carbonation with increasing cycle number.

6. Five-cycle test results using SBC Grade #3 at more severe calcination conditions of 200°C in atmospheres of pure CO_2 and 80%CO_2/20% H_2O were not significantly different than results at less severe standard calcination conditions.

3.1.2.2 Trona T-50 and T-200

1. All trona tests that examined the effect of reaction parameters using different samples for each run have been plagued with lack of reproducibility. Multicycle tests using the same trona sample showed improved reproducibility.

2. A five-cycle test using trona T-200 at standard calcination and carbonation conditions showed no loss of either reactivity or capacity over five cycles.

3. More severe calcination conditions (higher temperature and CO_2 atmosphere) caused greater losses in reactivity and capacity for both T-50 and T-200 than for SBC#3.

3.1.3 Experimental Procedure

3.1.3.1 Base Case Reaction Conditions

Base case reaction conditions 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, while not practical in commercial operation, were chosen to provide minimum severity of sorbent exposure during regeneration.

Table 1. Base Case Reaction Conditions For LSU TG Experiments.

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_2O
		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% CO_2, 16 mol% H_2O, balance He flowing at 600 scc/min and carbonation is continued until the reaction rate approaches zero. Appropriate changes in procedure are made when carbonation and calcination temperatures and gas compositions are altered from the base case.

3.1.3.2. <u>Testing Conducted During This Quarter</u>

Ten new multicycle electrobalance tests (eight five-cycle and two three-cycle), were completed during the quarter. These tests were designed to complete gaps in the data obtained in previous runs. Reaction conditions used in these tests are summarized in Table 2.

3.2 Fixed Bed Testing at LSU

In previous tests, the narrow operating temperature window and the difficulty in achieving H_2O vaporization at the 70°C carbonation temperature have complicated fixed-bed reactor tests. If the preheat temperature was too low, the H_2O does not vaporize and no carbonation occurs. If the preheat temperature was too high, the gases entering the reactor exceed the maximum carbonation temperature. Reasonable success has been achieved in a limited number of fixed-bed runs. Material balance closure was good and prebreakthrough concentrations corresponded to approximately 50% to 60% CO_2 removal. This quarter, three fixed-bed tests, in which H_2O was added by bubbling feed gas through a wash bottle contained in a constant

temperature bath at 56°C, were completed. This temperature produced the desired carbonation feed gas composition assuming that the product gas reached saturation.

Table 2. Conditions for Electrobalance Tests Conducted this Quarter at LSU.

Sorbent Precursor	Calcination		Carbonation Gas Composition,%	Number of Cycles
	Temp (°C)	Atm	$CO_2/H_2O/He/SO_2/O_2$	
SBC-1	160	He	8/16/76/0/0	5
SBC-1	120	He	8/16/76/0/0	5
SBC-1	200	CO_2	8/16/76/0/0	5
SBC-3	120	He	8/16/75.6/0.4/0	3
SBC-3	120	He	8/16/75.8/0.2/0	3
SBC-3	120	He	8/16/75.9/0.1/0	5
T-200	120	He	8/16/75.9/0.1/0	5
SBC-3	120	He	8/16/75.9/0.1/0	5
SBC-3	120	He	8/16/74.2/0.1/1.7	5
SBC-3	120	He	8/16/73.9/0.1/2	5

3.3 Sorbent Preparation at RTI

Two supported sorbents were prepared this quarter: 7.5% sodium carbonate and 40% sodium bicarbonate. The physical properties of these materials were determined and they will be subjected to TGA testing in the next quarter.

3.4 Fluidized Bed Reactor System Assembly at RTI

A 1-inch diameter quartz fluidized bed reactor system was designed and assembed for use in determining the fate of SO_2 and HCl containing simulated flue gases. The total length of the quartz reactor is 48-in. 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 known quantities of gas. 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 an HPLC 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 reactor system is shown schematically in Figure 1.
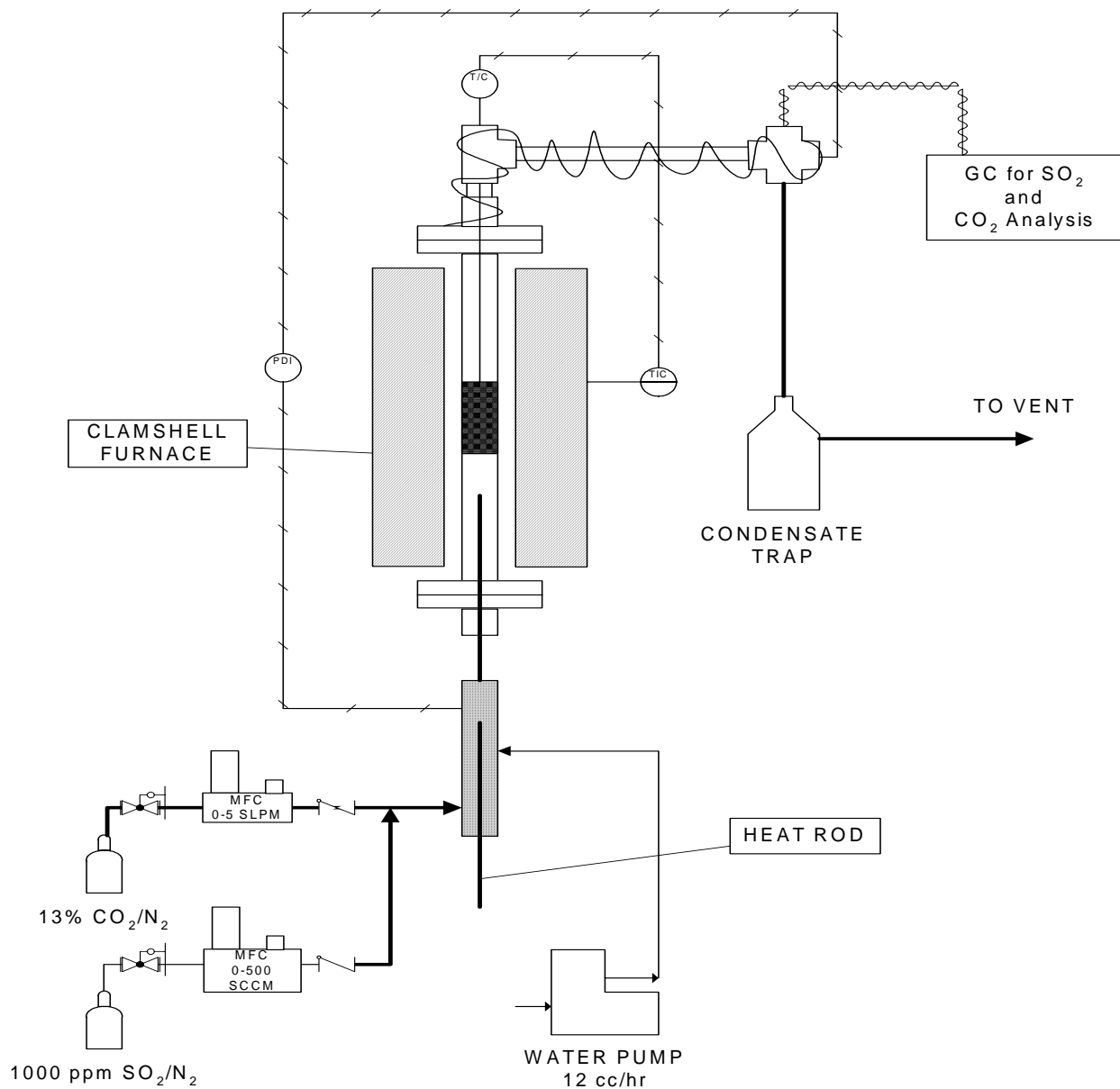

Figure 1. Schematic of quartz tube fluidized bed reactor system.

For testing involving SO_2, the reactor effluent will be directed to a gas chromatograph (GC). For testing of HCl, the reactor effluent will pass through an alkaline impinger solution for subsequent chemical analysis.

3.5 Thermogravimetric Analysis at RTI

RTI conducted TGA carbonation studies of 40% supported potassium carbonate with and without high temperature precalcination and 100% analytical grade potassium carbonate in different atmospheres. In addition a baseline test of the capacity of the spray dried support material without addition of sorbent was conducted.

4.0 RESULTS AND DISCUSSION

4.1 Electrobalance Testing at LSU

Tests were conducted on SBC#1, for comparison with base case tests on SBC#3. Both SBC#1 and SBC#3 are effectively 100% $NaHCO_3$. However, SBC#3 is composed of smaller particles as shown in Table 3 (Green et al., 2001a).

Table 3. Particle Size Distribution of SBC Grades 1 and 3 (% mass).

Particle Size, μ	SBC-1	SBC-3
+125	0.00	0.00
-125+88	8.56	1.03
-88+75	19.86	0.69
-75+53	43.84	10.31
-53	27.74	87.97

Figure 2 shows the dimensionless weight versus time results for five cycles using SBC-1 at standard calcination conditions, i.e., 120°C in He. It is immediately obvious that the first cycle results in the smallest reactivity and the largest capacity. Overall there appears to be little, if any, loss in activity through the five cycles.

Figures 3 and 4 show reactivity and capacity, f(25) and f(150), for the three tests using SBC-1. Note that fractional extents of reaction are based on Wegsheider's salt at the product (Green, et al. 2002). Figure 3 clearly shows an increase in activity through the first three cycles followed by a small decrease in cycles 4 and 5 following calcination at 120°C in He. It is also clear that higher calcination temperature has an adverse effect on multicycle activity, but that there is little, if any, activity decrease with increasing cycle number at any of the calcination conditions. It is also interesting to note that there is relatively little difference between the activity following calcination at 160°C in He and 200°C in CO_2.
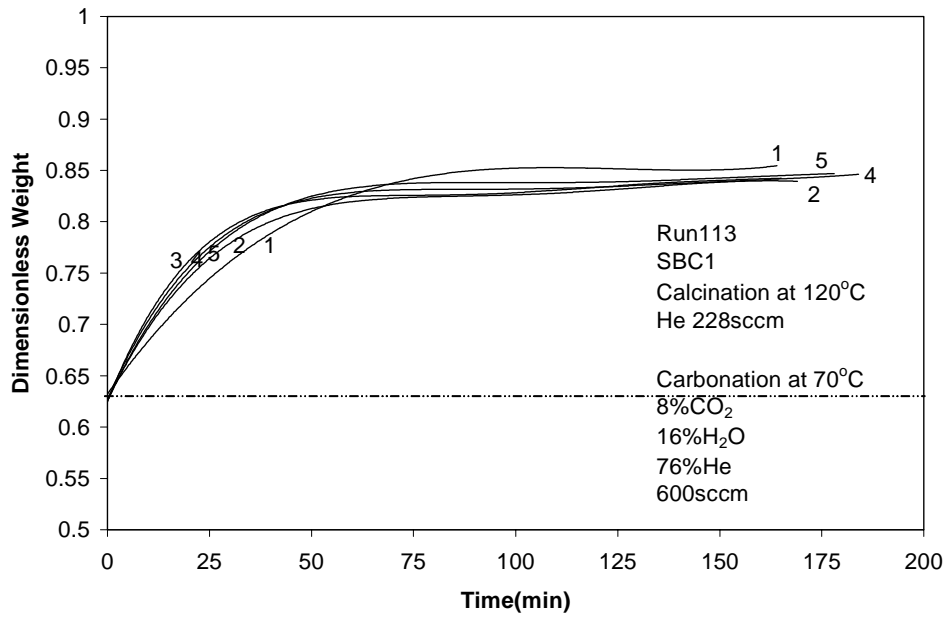
7

Figure 2. **Dimensionless weight versus time for five carbonation cycles using SBC#1: standard calcination and carbonation conditions.**
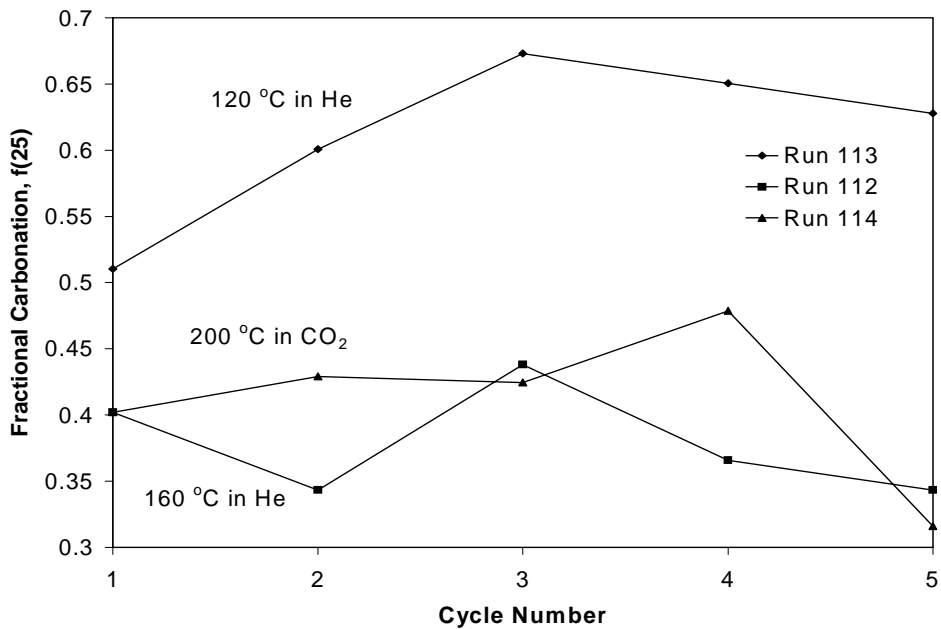

Figure 3. **Reactivity versus cycle number for three SBC-1 tests using different calcination conditions.**
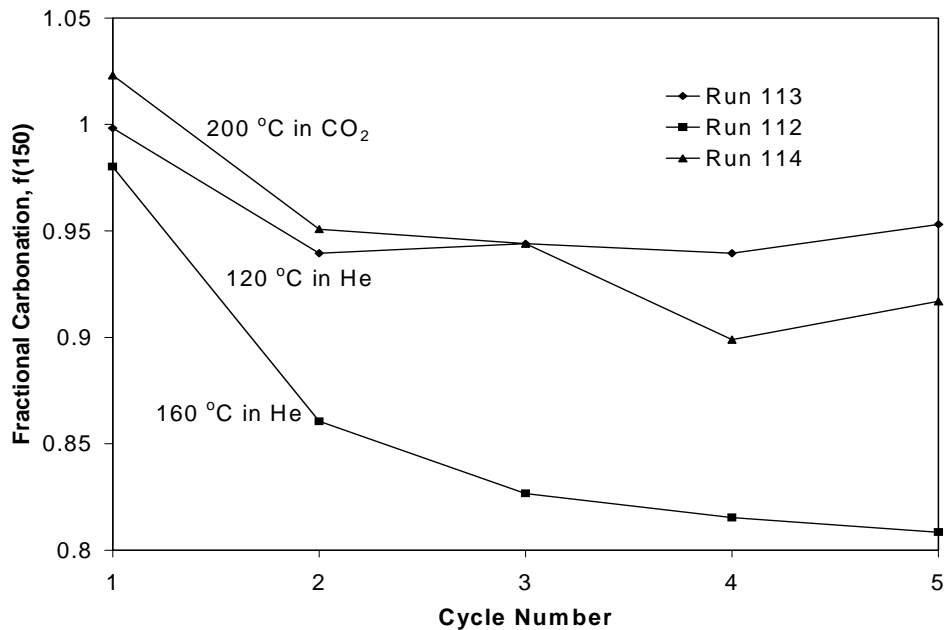
Figure 4. Sorbent capacity versus cycle number for three SBC-1 tests using different calcination conditions.

The sorbent capacity results shown in Figure 4 indicate little difference between calcination conditions of 120°C in He and 200°C in CO_2 on subsequent carbonation capacity. Both of these capacities are considerably larger than those obtained following calcination at 160°C in He. Further, after a large decrease in capacity between cycles 1 and 2 following 160°C calcination in He, there was relatively little further decrease in subsequent cycles.

Figures 5 and 6 compare reactivity and capacity for four sorbents: SBC#1, SBC#3, trona T-50, and trona T-200, following calcination at 160°C in He. These same figures appeared in the previous quarterly report (Green, et al., 2002) with data from SBC#3, T-50, and T-200; the current data for SBC#1 have now been added. SBC#1 clearly exhibits the highest activity while the capacities of SBC#1 and SBC#3 are approximately equal. Both show higher capacity than the trona samples. Losses in reactivity, with the exception of SBC#3 between cycles 1 and 2, and in capacity at all conditions, were moderate.

The presence of SO_2 in the flue gas will likely interfere with CO_2 removal through the formation of Na_2SO_3 and/or Na_2SO_4. The anticipated reactions are:

$$Na_2CO_3 + SO_2 \rightarrow Na_2SO_3 + CO_2 \qquad (7)$$

and,

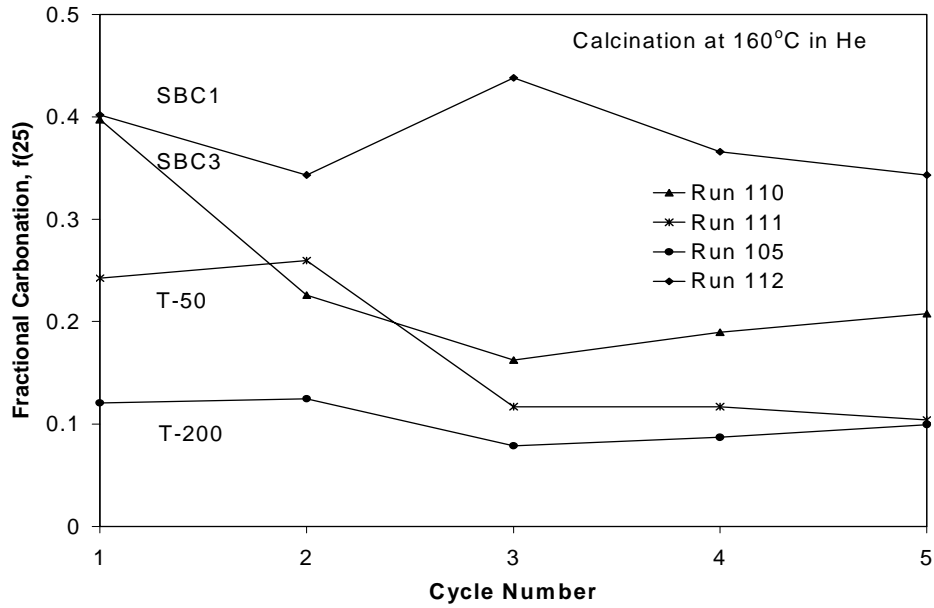$$Na_2CO_3 + SO_2 + \tfrac{1}{2}O_2 \rightarrow Na_2SO_4 + CO_2 \qquad (8)$$

9

Figure 5. Comparison of the performance of SBC#1, SBC#3, T-50, and T-200: f(25) versus cycle number following 160°C calcination in He.
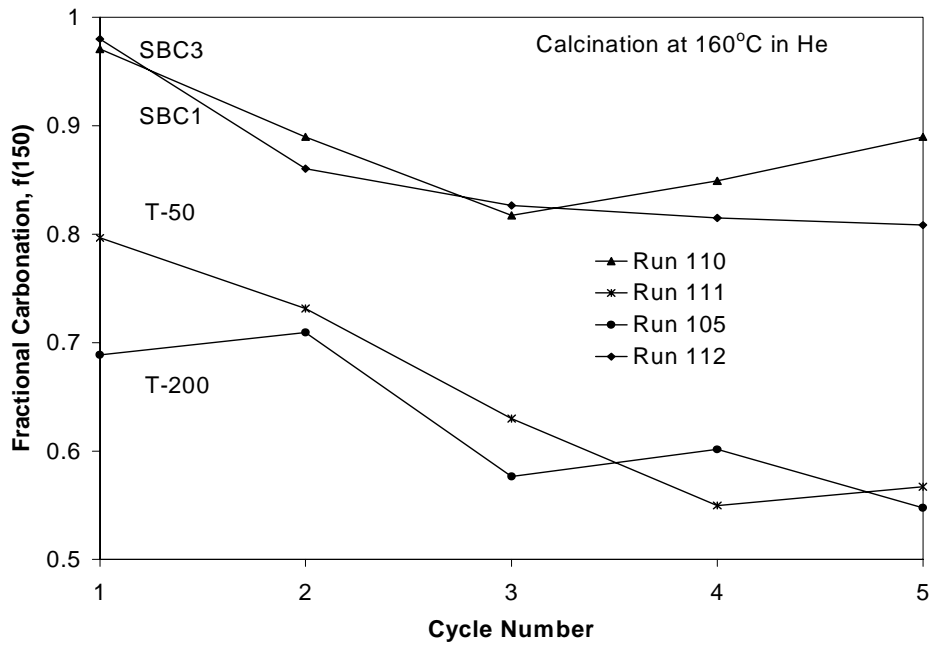

Figure 6. Comparison of the performance of SBC#1, SBC#3, T-50, and T-200: f(150) versus cycle number following 160°C calcination in He.

The effect of SO_2 addition, with and without the presence of free O_2, was examined in the remaining multicycle electrobalance tests. When 0.4% and 0.2% SO_2 were added, the tests were terminated after three cycles. The remaining tests, in which 0.1% SO_2 was added, were carried out through the complete five cycles. Standard calcination conditions and carbonation temperature were used in each test. Only the carbonation gas composition was varied. SBC#3 was used in six tests, and T-50 was used in one.

Figure 7 shows raw electrobalance data for a three-cycle test in which 0.2% SO_2 (no O_2) was added to the carbonation gas. The initial calcination progressed as expected with a final dimensionless weight very near the theoretical value of 0.631. The dimensionless weight increased rapidly during the first carbonation cycle and reached a maximum of about 0.88 slightly more than 100 minutes later. The dimensionless weight then began to decrease to about 0.83 when the carbonation cycle was ended. The final dimensionless weight at the end of the second calcination cycle was only 0.68. In the second carbonation cycle the maximum dimensionless weight was only about 0.82. The minimum weight following the third calcination was 0.71 and the maximum weight at the end of the third carbonation was 0.78. When the sorbent was calcined for a fourth time the final weight was only about 0.74. The calcination temperature was then increased to 200°C and little, if any, additional weight loss occurred. These results suggest the formation of increasing amounts of Na_2SO_3 during each carbonation cycle. Further it appears that the Na_2SO_3 is stable in He at temperatures as high as 200°C.
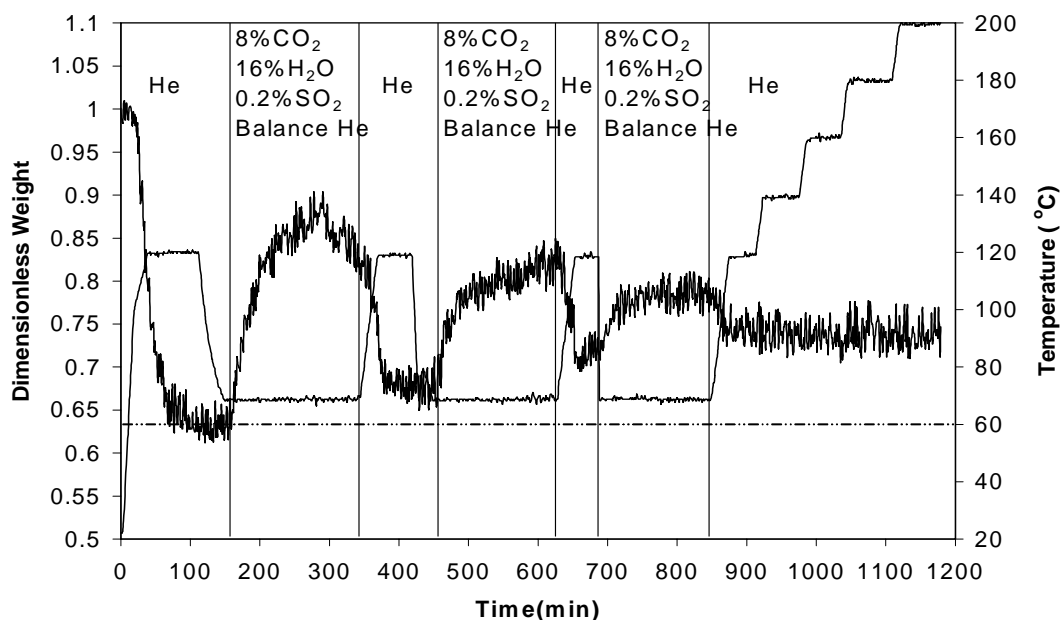

Figure 7. Dimensionless weight of SBC#3 versus time showing the effect of 0.2% SO_2 in the carbonation gas.

11

The cause of the maximum in the dimensionless weight, which occurred only during the first carbonation cycle, is unknown. The amount of CO_2 removed in each cycle should be proportional to the difference in dimensionless weight at the end of the carbonation and subsequent calcination cycles. The difference decreased from 0.15 in cycle 1 (based on the final dimensionless weight of 0.83) to 0.11 in cycle 2 to 0.04 in cycle 3. Clearly there was little CO_2 removal capacity left after three cycles.

Decreasing the SO_2 concentration to 0.1% produced qualitatively similar results, as is shown in Figure 8. However the reduction in SO_2 capacity occurred at a slower rate thus allowing five cycles to be completed. Note that no dimensionless weight maxima were observed during any of the carbonation cycles of Figure 8. The difference in dimensionless weight at the end of carbonation cycle 1 and calcination cycle 2 was about 0.17. At the end of four cycles this difference decreased to 0.06. These numbers suggest that the loss in CO_2 capacity following three cycles with 0.2% SO_2 in the feed gas was almost 75%, compared to an approximate 65% loss following four cycles with 0.1% SO_2 in the feed gas. Results of the test using trona T-200 with 0.1% SO_2 in the feed gas were qualitatively similar to those for SBC#3, as shown in Figure 8.
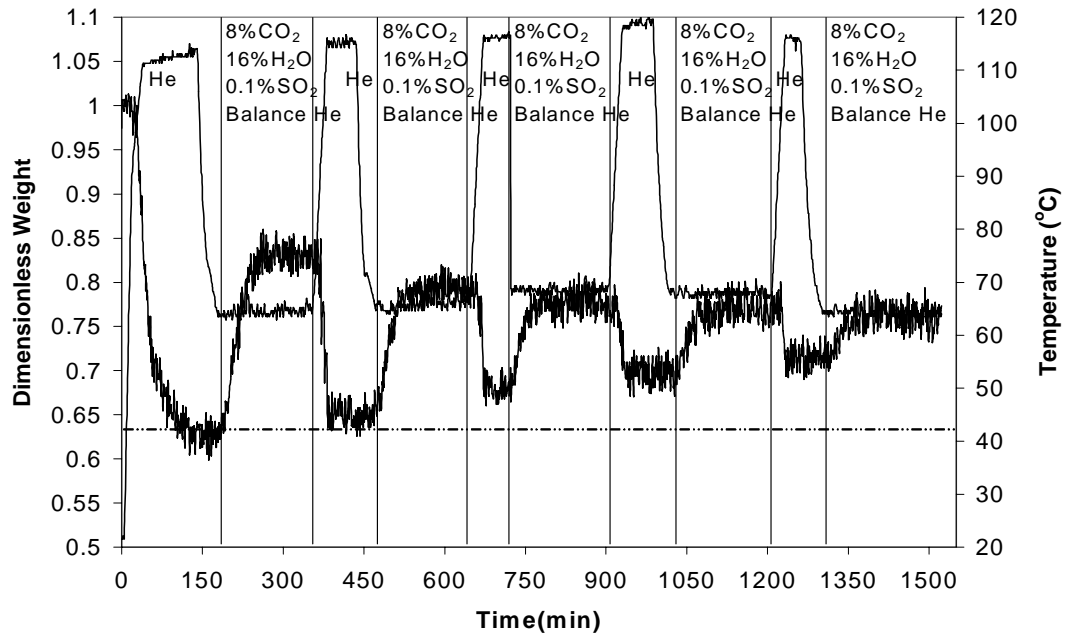
Figure 8. Dimensionless weight of SBC#3 versus time showing the effect of 0.1% SO_2 in the carbonation gas.

Results obtained when O_2 and SO_2 were added to the carbonation gas were not greatly different from results with SO_2 alone as shown in Figure 9. This figure shows five cycle results using SBC#3 with 0.1% SO_2 and 2.0% O_2 added to the carbonation gas. The loss in CO_2 capacity (again measured by the loss in dimensionless weight following carbonation) was also about 65% following four cycles.

12

The figure shows gas phase labels across the top: repeated blocks of "8%CO₂ 16%H₂O 0.1%SO₂ 2%O₂ Balance He" alternating with "He" regions. Y-axis left: Dimensionless Weight (0.5 to 1.1). Y-axis right: Temperature (°C) (20 to 120). X-axis: Time(min) 0 to 1500.
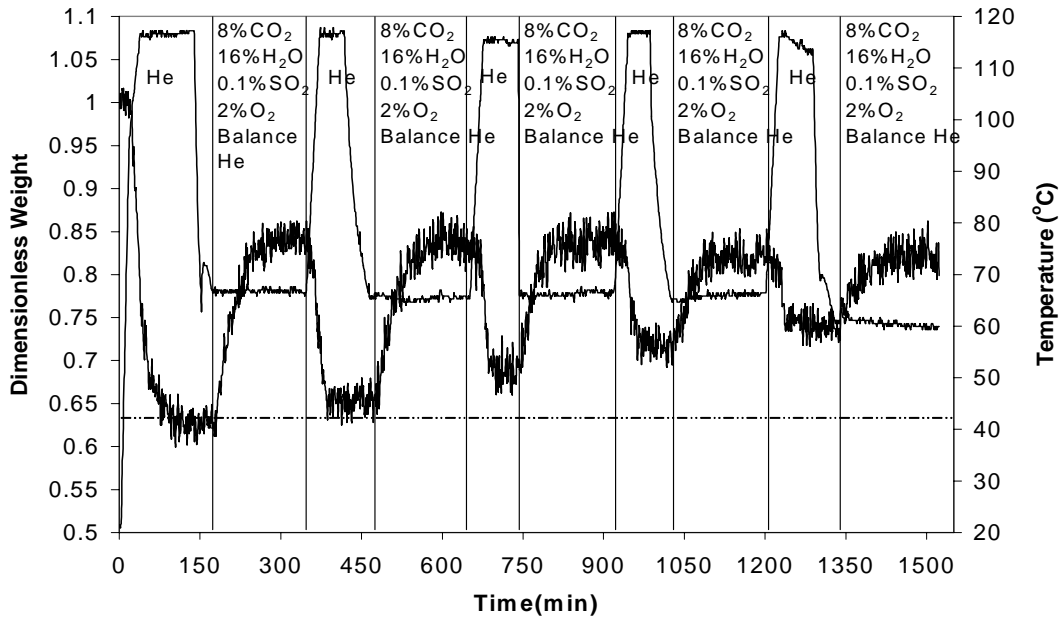
Figure 9. **Dimensionless weight of SBC#3 versus time showing the effect of 0.1% SO₂ plus 2.0% O₂ in the carbonation gas.**

4.2 Fixed Bed Reactor Testing at LSU

Three fixed bed tests were conducted this quarter. In the first test (consisting of two calcination cycles and one carbonation cycle), SBC#3 was used with a total carbonation gas feed rate of 300 scc/min. Results of this test are shown in Figure 10.

The material balance closure was generally good. Complete calcination of the initial SBC#3 charge was expected to produce 0.149 mol of CO_2, and numerical integration of the area under the CO_2-time curve corresponds to 0.142 mols of CO_2. During carbonation the CO_2 concentration (dry basis) was about 6.3%, corresponding to roughly 40% CO_2 removal, for approximately 100 minutes. The CO_2 concentration then gradually increased to about 9.8% (dry basis). Numerical integration of the area above the CO_2 breakthrough curve shows that approximately 0.084 mols of CO_2 were removed during carbonation. This value is about 56.6% of theoretical based on $NaHCO_3$ as the product and about 94.4% of theoretical based on Wegscheider's salt product. Finally, the area under the CO_2 curve produced during the second calcination corresponds to 0.075 mols, which is approximately 10% less than the amount removed during carbonation.

The only serious problem with this test was that the postbreakthrough CO_2 concentration approached 9.8% (dry basis) compared to a theoretical value of 9.5% corresponding to the dry feed gas. This may indicate that the feed gas emerging from the wash bottle was not completely saturated. The 9.8% CO_2 (dry basis) corresponds to wet basis concentrations of 8.2% CO_2 and 14.2 % H_2O, compared to the target values of 8.0% CO_2 and 16% H_2O. The result of this test is, however, significantly better than the test result reported in the last

13

quarterly report (Green, et al. 2002) where the steady-state postbreakthrough CO_2 concentration was 11.4% (dry basis).

Figure 10. Fixed-bed reactor test: CO_2 concentration as a function of time during a 1.5 cycle test with a total carbonation feed rate of 300 scc/min.

The total gas feed rate was reduced to 150 scc/min in the other fixed-bed tests to provide increased gas-sorbent contact time and, hopefully, increased CO_2 removal. Results of the second 1.5 cycle test are shown in Figure 11. The experimental value of CO_2 produced during the first calcination, 0.15 mols, was equal to the theoretical value. During carbonation, 0.084 mols of CO_2 were removed and 0.083 mols of CO_2 were liberated during the second calcination period. The problem with this test was the uneven CO_2 concentrations measured during the prebreakthrough carbonation period, ranging from about 3.0% to 5.5%. These values correspond to an average of about 50% CO_2 removal during prebreakthrough.
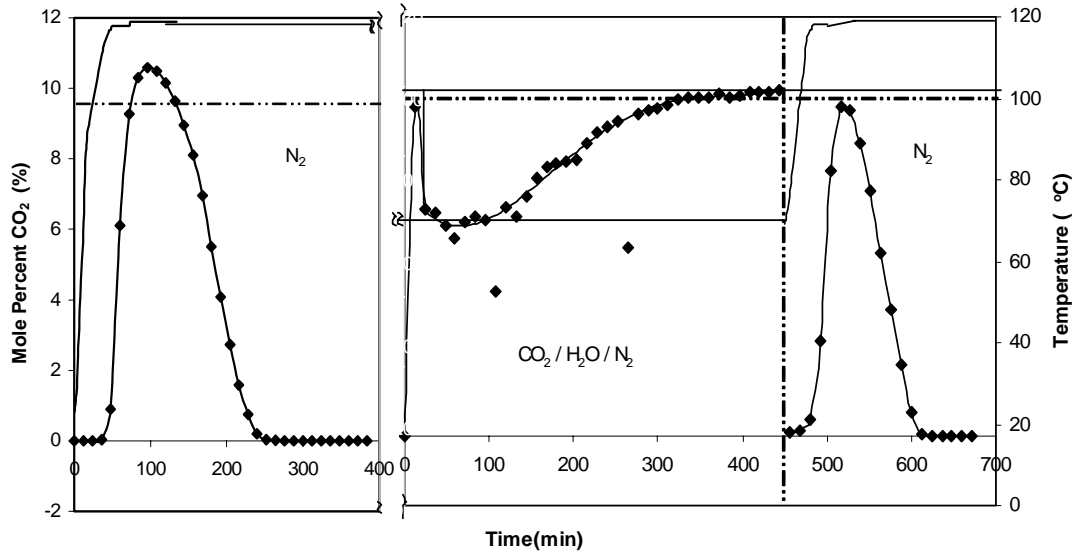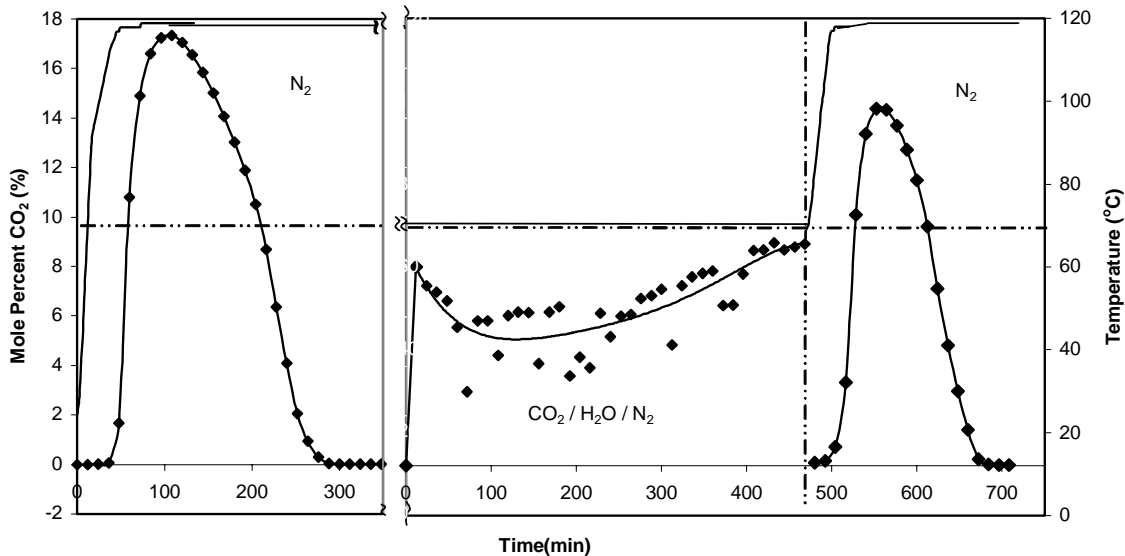
Figure 11. Fixed-bed reactor test: CO_2 concentration as a function of time during a 1.5 cycle test with a total carbonation feed rate of 150 scc/min.

4.3 Thermogravimetric Analysis Testing at RTI

4.3.1 Testing of Supported Sorbent Material

The 40% supported potassium carbonate material was subjected to a three cycle test. The material was dried at in helium at 105°C prior to the first carbonation, and calcined in dry nitrogen at 150°C between carbonation cycles. Carbonation took place at 70°C in a gas composed of 6.5% water vapor and 7.5% carbon dioxide. Based on normalized weight of dry material, weight gains of 0.3%, 0.4% and 0.1% were obtained for the three carbonations. The results are shown in Figure 12.

Stoichiometric conversion of the potassium carbonate material to potassium bicarbonate would produce an increase in weight of about 18%. The decreased activity of the sample may have been due to a lower than expected water content of the carbonation gas. For this experiment, water vapor was added by bubbling part of the carbonation gas through an impinger, and the contact may have been insufficient for the gas to reach saturation. Alternately, the supported material may have deteriorated through exposure to the atmosphere.
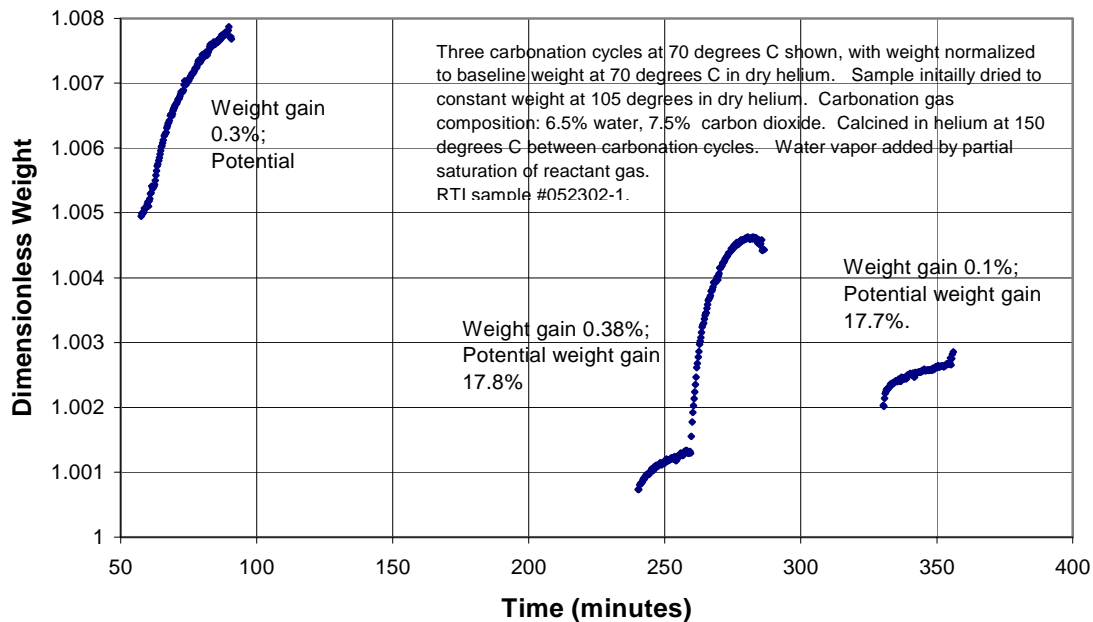
15

The chart contains the following labels:

- Y-axis: **Dimensionless Weight** (values 1, 1.001, 1.002, 1.003, 1.004, 1.005, 1.006, 1.007, 1.008)
- X-axis: **Time (minutes)** (values 50, 100, 150, 200, 250, 300, 350, 400)

Text within chart:

"Weight gain 0.3%; Potential"

"Three carbonation cycles at 70 degrees C shown, with weight normalized to baseline weight at 70 degrees C in dry helium.   Sample initailly dried to constant weight at 105 degrees in dry helium. Carbonation gas composition: 6.5% water, 7.5% carbon dioxide. Calcined in helium at 150 degrees C between carbonation cycles.   Water vapor added by partial saturation of reactant gas. RTI sample #052302-1."

"Weight gain 0.38%; Potential weight gain 17.8%"

"Weight gain 0.1%; Potential weight gain 17.7%."

Figure 12. Carbonation of 40% supported potassium carbonate at 70 degrees C.

A fresh sample of material was precalcined in helium at 400°C before carbonation in a gas containing 4.0% water vapor and 8.0% carbon dioxide at 80°C. In this run, a syringe pump was used to add water to the carbonation gas. A very rapid initial reaction rate was observed, however the weight gain leveled off at 3.9%. Results of this test are shown in Figure 13.

4.3.2 Testing of Support Material

In order to determine the contribution that adsorption of gases by the support material made to the total weight gain observed in the carbonation tests conducted on the supported sorbent material, a sample of support material with no active sorbent incorporated was tested. Results are shown in Figure 14. The support was dried at 105°C and then cooled to 60°C. This produced a weight loss of 2.2%. Taking the dry 60°C weight as a baseline, the sample was then exposed to 20% CO_2 in nitrogen. This produced a weight gain of 2.2%, presumably due to adsorption on CO_2. This apparent weight gain was decreased by 0.25% upon heating to 80°C, and a further 0.25% upon heating to 100°C. An additional 0.25% reduction in the weight loss was observed when the atmosphere was isothermally switched to pure dry nitrogen.
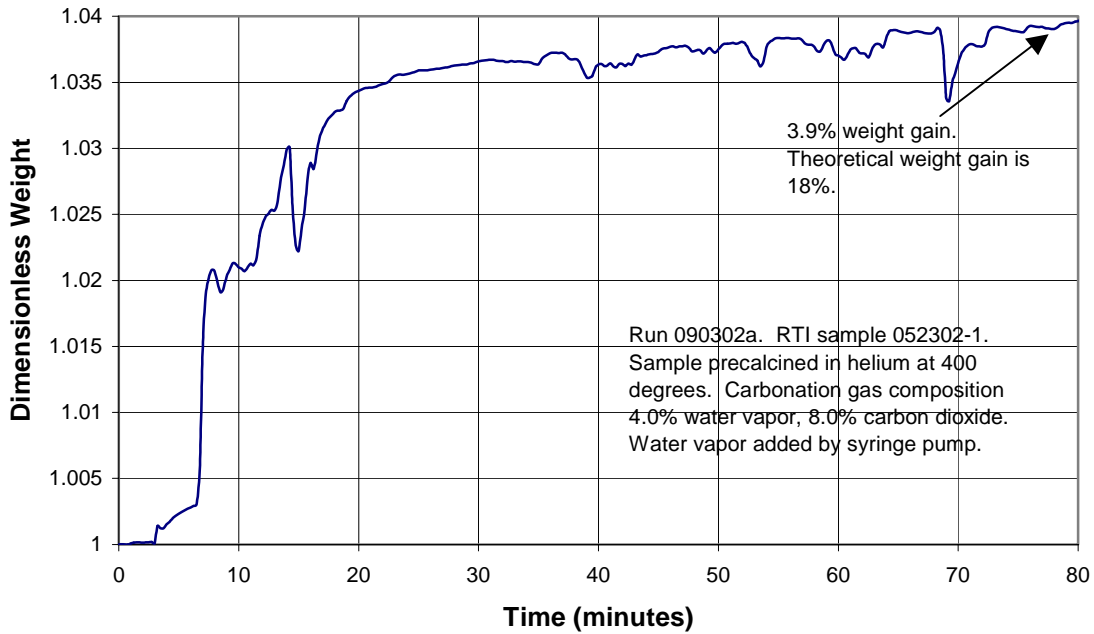
16

Figure 13. Carbonation of precalcined 40% supported potassium carbonate at 80 degrees.
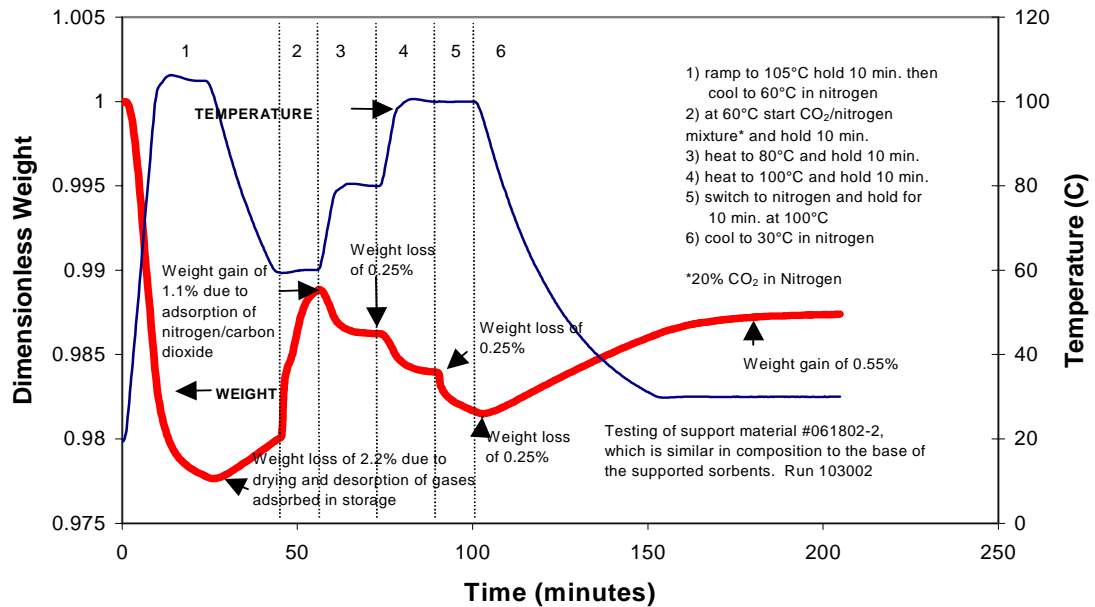

Figure 14. Adsorption profile of support material.

17

These changes in mass upon increase in temperature are thought to be caused by progressively lower adsorption capacities of the sorbent. The direction of the changes (to this point in the run) is counter to that expected from potential buoyancy-resultant instrumental biases. The final stage of the run involved cooling in nitrogen back to 30°C. The weight gain of 0.55% observed in this stage of the run may be due to adsorption of nitrogen (in which case, nitrogen adsorption was probably significant in the earlier stages), or the previously mentioned instrumental bias. In any event, weight changes of this magnitude are significant when considered against the relatively small weight changes observed in testing of the supported sorbent materials.

4.3.3 <u>Testing of Potassium Carbonate</u>

Two carbonation tests were conducted with analytical grade potassium carbonate at 80°C. The samples were dried to constant weight before starting the carbonation gas which contained 8% CO_2. The tests were continued for about 2 hours with water vapor contents of 4% and 6%. A slightly greater increase in weight was observed in the test with the higher water vapor content. Results are shown in Figure 15.
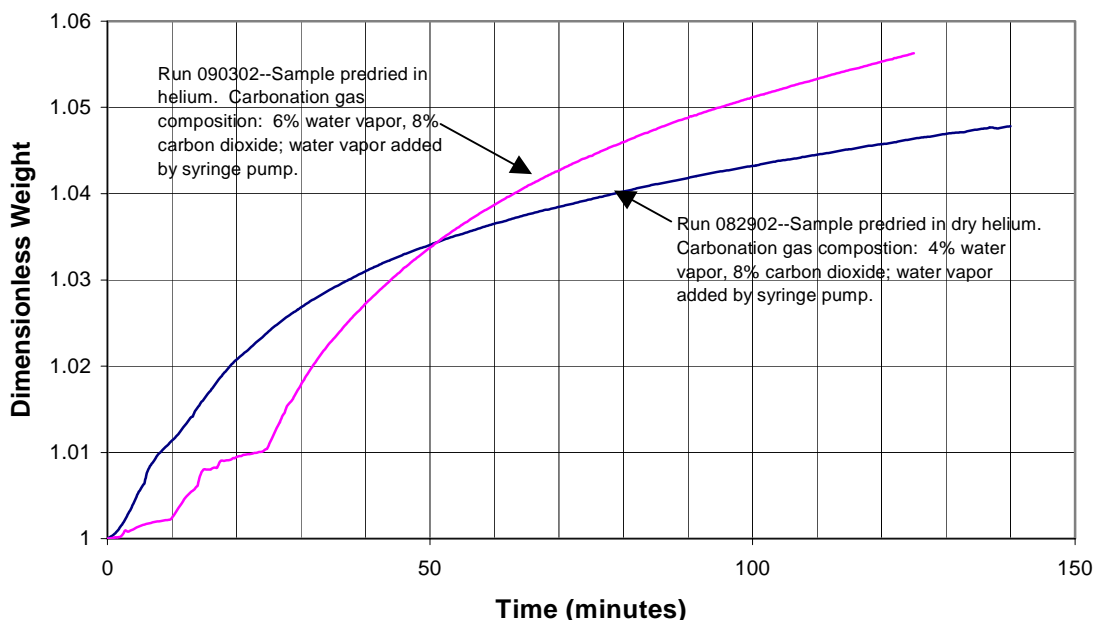

Figure 15. Carbonation of potassium carbonate at 80 degrees C.

4.4 Preparation and Testing of Additional Sorbent Materials

RTI investigated three supported sodium carbonate materials this quarter. Two materials, composed of 20% and 40% sodium carbonate were prepared by spray drying. A 7.5% sodium

carbonate material was prepared by saturating a support material and subsequent drying. Jet cup attrition testing (ASTM, 1995) of the 20% material indicated that it was unsuitable for transport reactor processing. Selected properties determined this quarter for this and other materials is given in Table 4. The 7.5% supported material has a relatively high BET surface area, consistent with the alumina based support material used to produce it.

Table 4. Selected Properties of Additional Sorbent Precursors

	20% Supported Sodium Carbonate (90402-1)	40% Supported Sodium Carbonate (121702-1)	7.5% Supported Sodium Carbonate (110102-1)	Spherical Sodium Bicarbonate	Jet Milled Potassium Carbonate
Jet Cup Attrition Index	8.7	N/A	N/A	8.7	N/A
BET Surface Area (sq. m/g)	N/A	5.84	177.9	4.88	2.2
Compact Bulk Density (g/cc)	N/A	0.95	N/A	N/A	0.861
Hg Pore Data					
TOTAL INTRUSION VOLUME (cc/g)	N/A	0.1042	N/A	N/A	0.0372
TOTAL PORE AREA (sq. m/g)	N/A	21.696	N/A	N/A	17.434
MEDIAN PORE DIAMETER (VOLUME) ÅÅ	N/A	529	N/A	N/A	102
MEDIAN PORE DIAMETER (AREA) ÅÅ	N/A	61	N/A	N/A	50
AVERAGE PORE DIAMETER (4V/A) ÅÅ	N/A	192	N/A	N/A	85
BULK DENSITY (g/cc)	N/A	1.7498	N/A	N/A	1.9843
APPARENT (SKELETAL) DENSITY (g/cc)	N/A	2.1403	N/A	N/A	2.1423
POROSITY (%)		18.2414			7.3746
Particle Size Data					
+150	N/A	25.00	N/A	N/A	N/A
-150+125	N/A	6.69	N/A	N/A	N/A
-125+90	N/A	16.20	N/A	N/A	N/A
-90+75	N/A	9.51	N/A	N/A	N/A
-75+53	N/A	23.59	N/A	N/A	N/A
-53+38	N/A	14.08	N/A	N/A	N/A
-38	N/A	4.93	N/A	N/A	N/A

Church and Dwight provided two other materials, a spherical sodium bicarbonate, described in the previous quarterly report (Green, et al. 2002) and a jet-milled potassium carbonate. Attrition testing of the spherical sodium bicarbonate indicated that it would offer no advantages over the previously tested grades. Additional testing of the jet milled potassium carbonate will take place in the next quarter.

4.5 Other Project Activities

Dr. Harrison presented a paper, "Carbon Dioxide Capture From Flue Gas Using Dry Regenerable Sorbents", at the "Future Energy Systems and Technology for CO_2 Abatement" conference held in Antwerp, Belgium on November 18, 2002.

5.0 CONCLUSIONS AND FUTURE WORK

High calcination temperatures decrease the activity of sodium bicarbonate Grade 1 (SBC#1) during subsequent carbonation cycles, but there is little or no progressive decrease in activity in successive cycles. SBC#1 appears to be more active than either SBC#3 or the two grades of trona tested previously. As expected, the presence of SO_2 in simulated flue gas results in a progressive loss of sorbent capacity with increasing cycles. After three cycles with 0.2% SO_2 in the carbonation feed gas, the CO_2 capacity of calcined SBC#3 decreased by about 75%. This is most likely due to an irreversible reaction to produce Na_2SO_3. This compound appears to be stable at calcination temperatures as high as 200°C.

Tests of 40% supported potassium carbonate sorbent and plain support material suggest that some of the activity observed in tests of the supported sorbent may be due to adsorption by the support material rather than to carbonation of the sorbent.

During the next quarter, LSU will examine the effects of temperature and feed gas flow rate on sorbent activity in multicycle fixed bed reactor tests. RTI will examine the effect of SO_2 and HCl on sorbent capacity in the 1-inch diameter quartz fluidized bed reactor system.

6.0 REFERENCES

ASTM, International, Method D5757-95: Standard Test Method for Determination of Attrition and Abrasion of Powdered Catalysts by Air Jets. 1995

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).

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

Green, D.A., Turk, B.S., Portzer, J. W., Gupta, R., McMichael, Harrison, D.P., and Liang, Y., Carbon Dioxide Capture From Flue Gas Using Dry Regenerable Sorbents, Quarterly Technical Progress Report, Research Triangle Institute, October 2002.