

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	iv
List of Tables	v
1.0 EXECUTIVE SUMMARY	1
2.0 INTRODUCTION	1
3.0 EXPERIMENTAL	2
3.1 Electrobalance Testing at LSU	2
3.1.1 Sorbents Used	2
3.1.2 Previous Experimental Results	2
3.1.3 Experimental Conditions	3
3.2 Fixed Bed Testing at LSU	3
3.3 Fluidized-Bed Reactor Testing at RTI	3
3.3.1 Testing Conducted This Quarter	3
3.3.2 Reactor Modifications	4
4.0 RESULTS AND DISCUSSION	4
4.1 Electrobalance Testing at LSU	4
4.1.1 Five-Cycle Testing Results	5
4.2 Fixed Bed Reactor Tests at LSU	9
4.3 Fluidized Bed Testing at RTI	11
4.4 Thermodynamic Analysis of Sodium Carbonate Phases	13
5.0 CONCLUSIONS AND FUTURE WORK	24
6.0 REFERENCES	25

LIST OF FIGURES

Figure	Page
1 Fixed-bed reactor system at LSU	4
2 Raw electrobalance data for five-cycle test using calcination at 200°C in pure CO ₂	5
3 Smoothed electrobalance data for 5-cycles using calcination at 200°C in pure CO ₂	6
4 Fractional conversion in 5-cycle test with SBC Grade #3 sorbent (calcination at 200°C in pure CO ₂)	7
5 Fractional conversion results from triplicate test with SBC Grade #3 (calcination at 120°C in pure He)	8
6 Fractional conversion results from two duplicate tests with SBC Grade #3 (calcination at 200°C in pure CO ₂)	8
7 Comparison of f(25) and f(150) results for three different calcination conditions	9
8 CO ₂ concentration in fixed bed reactor product gas stream	10
9 Temperature profile–Cycle 1 with Trona T-50	11
10 Cycle 1 carbonation test with Trona T-50	12
11 Temperature profile--Cycle 2 with Trona T-50	13
12 Cycle 2 carbonation test with Trona T-50	14
13 Effect of carbonation temperature using SBC grade #3	16
14 Equilibrium curves for a sodium carbonate - sodium bicarbonate system generated using the HSC chemistry software	18
15 Phase diagram for sodium carbonate/sodium bicarbonate system	19
16 Equilibrium constants for the sodium carbonate - sodium bicarbonate system using data obtained from Church and Dwight	20
17 Comparison of equilibrium constants for reactions 6, 9, & 14	21

LIST OF TABLES

Table		Page
1	Base Reaction Conditions	3
2	Summary of 2 Cycle Carbonation Test Data	12
3	Comparison of the Experimental and Computed Initial Conversion Rates of Na_2CO_3 to $\text{Na}_2\text{CO}_3 \cdot 3\text{NaHCO}_3$	22

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, or “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.

This quarter, five cycle thermogravimetric tests were conducted at the Louisiana State University (LSU) with sodium bicarbonate Grade 3 (SBC#3) which showed that carbonation activity declined slightly over 5 cycles following severe calcination conditions of 200°C in pure CO₂. Three different sets of calcination conditions were tested. Initial carbonation activity (as measured by extent of reaction in the first 25 minutes) was greatest subsequent to calcination at 120°C in He, slightly less subsequent to calcination in 80% CO₂/20% H₂O, and lowest subsequent to calcination in pure CO₂ at 200°C. Differences in the extent of reaction after 150 minutes of carbonation, subsequent to calcination under the same conditions followed the same trend but were less significant. The differences between fractional carbonation under the three calcination conditions declined with increasing cycles.

A preliminary fixed bed reactor test was also conducted at LSU. Following calcination, the sorbent removed approximately 19% of the CO₂ in the simulated flue gas. CO₂ evolved during subsequent calcination was consistent with an extent of carbonation of approximately 49%.

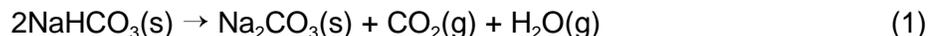
Following successful testing of SBC#3 sorbent at RTI reported in the last quarter, a two cycle fluidized bed reactor test was conducted with trona as the sorbent precursor, which was calcined to sodium carbonate. In the first carbonation cycle, CO₂ removal rates declined from 20% to about 8% over the course of three hours. Following calcination, a second carbonation cycle was conducted, at a lower temperature with a lower water vapor content. CO₂ removal and sorbent capacity utilization declined under these conditions. Modifications were made to the reactor to permit addition of extra water for testing in the next quarter.

Thermodynamic analysis of the carbonation reaction suggested the importance of other phases, intermediate between sodium carbonate and sodium bicarbonate, and the potential for misapplication of thermodynamic data from the literature. An analysis of initial rate data from TGA experiments suggested that the data may fit a model controlled by the heat transfer from the sorbent particle surface to the bulk 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 primary reactions, based upon the use of sodium bicarbonate as the sorbent precursor and sodium carbonate as the reaction product are:



and



Reaction (1) releases CO₂ and regenerates the sorbent, while Reaction (2) is used to capture CO₂. Several other solid products, intermediate between sodium carbonate and sodium bicarbonate, may also be produced under the anticipated reaction conditions.

This report describes activities conducted between October 1, 2001 and December, 31 2001 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 reaction studies at LSU, and fluidized-bed reactor testing and thermodynamic and kinetic analyses at RTI.

3.0 EXPERIMENTAL

3.1 Electrobalance Testing at LSU

3.1.1 Sorbents Used

Thermogravimetric analysis (TGA) testing was conducted at LSU with sodium bicarbonate Grade 3 (SBC#3). Selected properties of this material, 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 testing has been with SBC Grade #3 and with Trona T-50. Lack of reproducibility has plagued the T-50 results, and the following summary pertains primarily to SBC Grade #3.

- Both the initial reaction rate and achievable CO₂ capacity decrease with increasing carbonation temperature.
- The possible formation of by-products including Na₂CO₃•H₂O, Na₂CO₃•NaHCO₃•2H₂O, and Na₂CO₃•3NaHCO₃ at carbonation conditions of potential interest was proven by thermodynamic analysis.

- At constant temperature the global reaction rate increases with an increase in both CO₂ and H₂O concentrations.
- 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 essentially constant in Cycles 3, 4, and 5.

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 changed from the base case.

3.2 Fixed Bed Testing at LSU

The LSU fixed bed reactor system, shown in Figure 1, was slightly modified during the quarter for use in calcination/carbonation reactions. One preliminary two cycle test was conducted in which approximately 20 g of SBC#3 sorbent was calcined in He at 120°C and then carbonated in 8% CO₂, 16% H₂O, balance He at 70°C.

3.3 Fluidized-Bed Reactor Testing at RTI

3.3.1 Testing Conducted This Quarter

RTI conducted a two cycle calcination/carbonation test using trona T-50 in a 2-inch internal diameter fluidized bed reactor system. Selected properties of this material, as-received and following calcination were also reported previously (Green, et al., 2001a,b). The reactor and

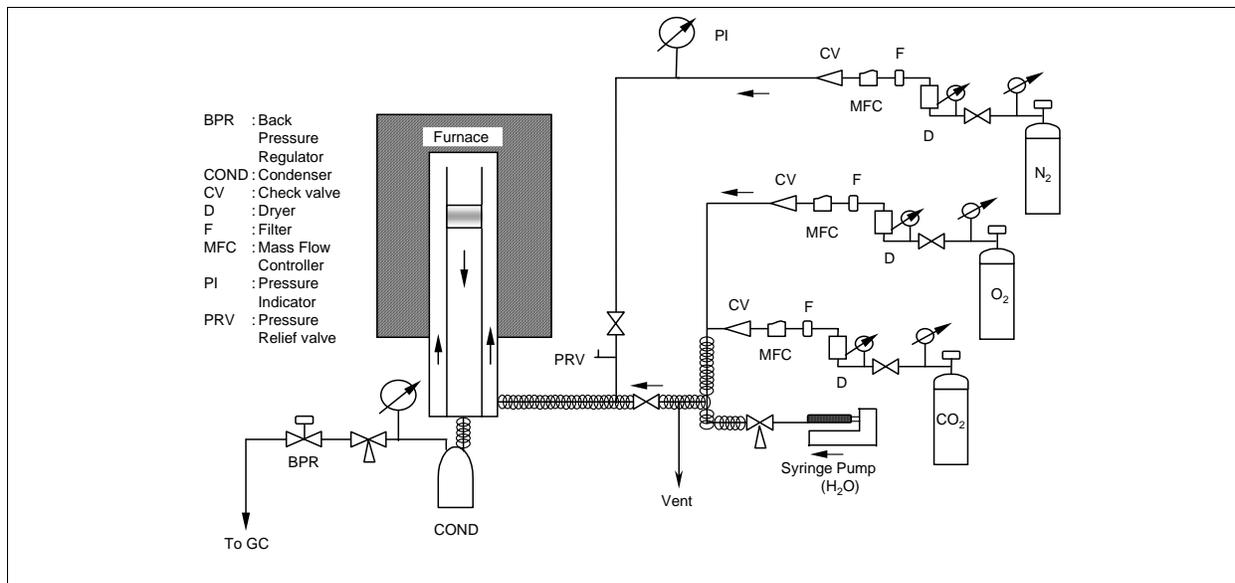


Figure 1. Fixed-bed reactor system at LSU.

associated instrumentation were also described in the previous quarterly report (Green, et al., 2001d) with the exception that the oxygen sensor was not used, as it was found to degrade in accuracy under the test conditions.

3.3.2 Reactor Modifications

Because the carbonation reaction rate is strongly dependent on the concentration of H₂O in the simulated flue gas, and because the latent heat of vaporization of water can be used to reduce the temperature of the sorbent bed, provisions were made to add liquid water near the top of the fluidized bed for future tests. A 1/16-in outside diameter polytetrafluoroethane (PTFE) tube was inserted through the upper reactor flange and extended along the outside of the thermowell, to a height approximately 6-in above the flow distributor. A variable speed syringe pump was connected to the tube, to permit deionized water addition for fluidized bed tests to be conducted in the next quarter.

4.0 RESULTS AND DISCUSSION

4.1 Electrobalance Testing at LSU

Five electrobalance runs, each consisting of five complete calcination-carbonation cycles were completed during October and November. Each run used SBC Grade #3 and standard carbonation conditions of 70°C in 8% CO₂, 16% H₂O, balance He at 600 scc/min. The primary purpose was to evaluate the effect of calcination atmosphere and temperature on reactivity during the subsequent carbonation cycles. Pure He, pure CO₂, and a mixture of 80% CO₂/20% H₂O were used during calcination at temperatures of either 120°C or 200°C.

4.1.1 Five-Cycle Testing Results

Raw electrobalance results from a five-cycle test using SBC Grade #3 with calcination at 200°C in pure CO₂ are shown in Figure 2. The initial chemical form of the sorbent was NaHCO₃ and it is represented in Figure 2 as having dimensionless weight of 1.0. Initial calcination was complete after about 30 minutes as indicated by the constant dimensionless weight of ~0.63. Note that this final dimensionless weight was achieved at the end of all five calcination steps, indicating that the chemical form of the regenerated sorbent is sodium carbonate. Carbonation was initiated at ~180 minutes and continued until the final dimensionless weight of ~0.83, corresponding to fractional carbonation of ~0.56 (based on the conversion of sodium carbonate to sodium bicarbonate), was reached. In this test, the sample was left overnight at 70°C in pure He following each carbonation cycle, and the subsequent calcination and carbonation occurred the next day. As a result the time scale shown in Figure 2 is arbitrary following the first cycle. In some previous tests, multiple cycles were completed in a single day and it was suspected that the overall duration of the test period might have had an effect on carbonation activity.

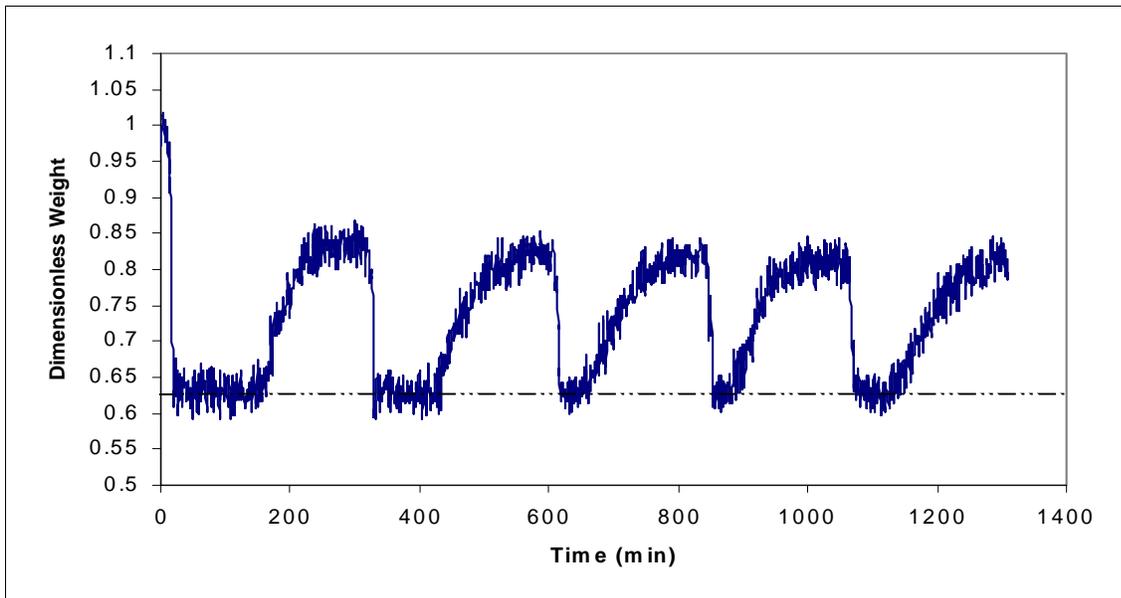


Figure 2. Raw electrobalance data for five-cycle test using calcination at 200°C in pure CO₂.

Careful study of the Figure 2 results shows small decreases in the slopes of the dimensionless weight-time curves near the beginning of carbonation and in the final dimensionless weight near the end of carbonation. Both are indicative of decreased activity with increasing number of cycles. These results are indicated more clearly in Figure 3 where smoothed electrobalance data during the five carbonation cycles are overlaid. Both the reduced slope and reduced final dimensionless weight are obvious.

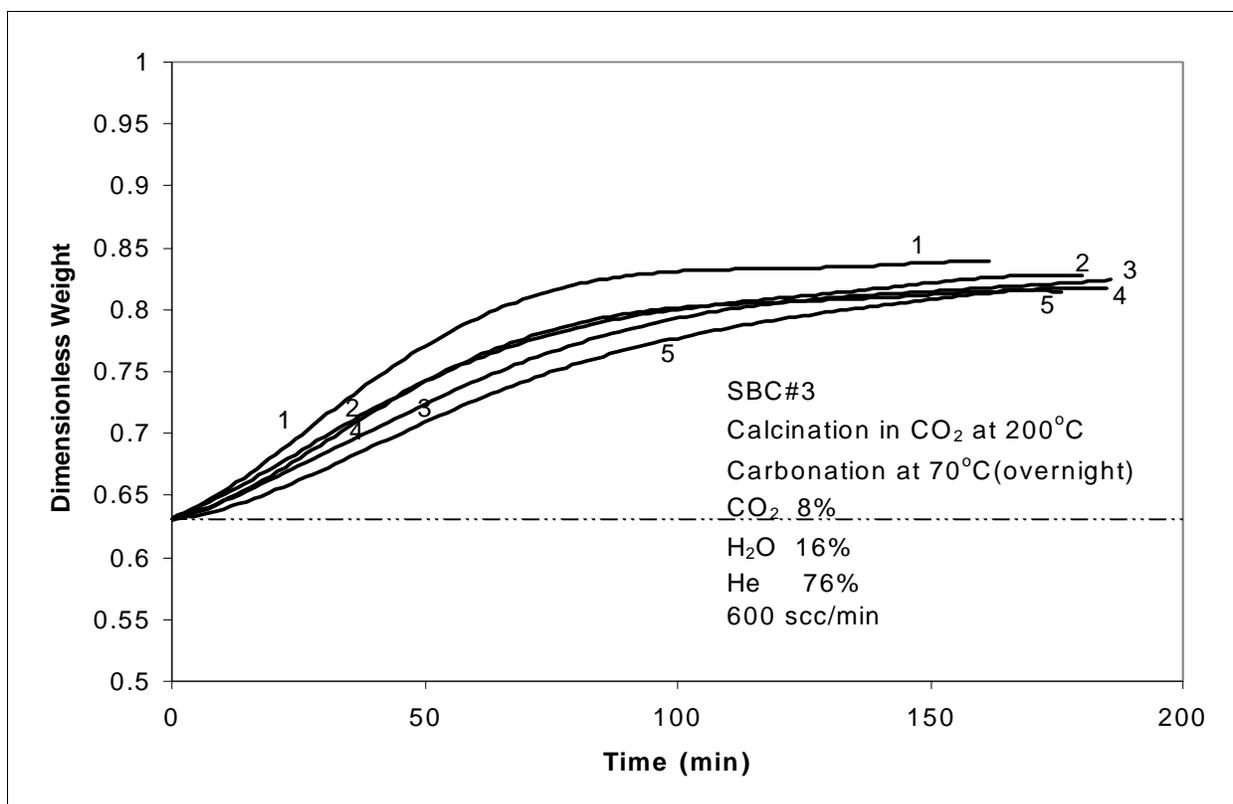


Figure 3. Smoothed electrobalance data for 5-cycles using calcination at 200°C in pure CO₂.

The data are represented by conversion of Na₂CO₃ to NaHCO₃ at selected times in order to facilitate comparison of results from different runs. In general, fractional conversion, $f(t)$, as a function of time is given by

$$f(t) = \frac{m(t) - 0.631}{0.369} \quad (3)$$

where $m(t)$ = dimensionless weight at time, t , and 0.631 and 0.369 are the theoretical dimensionless weight and dimensionless weight loss corresponding to complete calcination of 2NaHCO₃ to Na₂CO₃, respectively. In this analysis, $t = 25$ minutes and $t = 150$ minutes have been chosen as a measure of reaction rate and final conversion, respectively.

Values of $f(25)$ and $f(150)$ for the previous run are illustrated in Figure 4. There is a clear decrease in both reaction rate and final conversion from Cycles 1 to 2 to 3. However, the final conversion is effectively constant in Cycles 3, 4, and 5. The reaction rate increases between Cycles 3 and 4 and then decreases between Cycles 4 and 5.

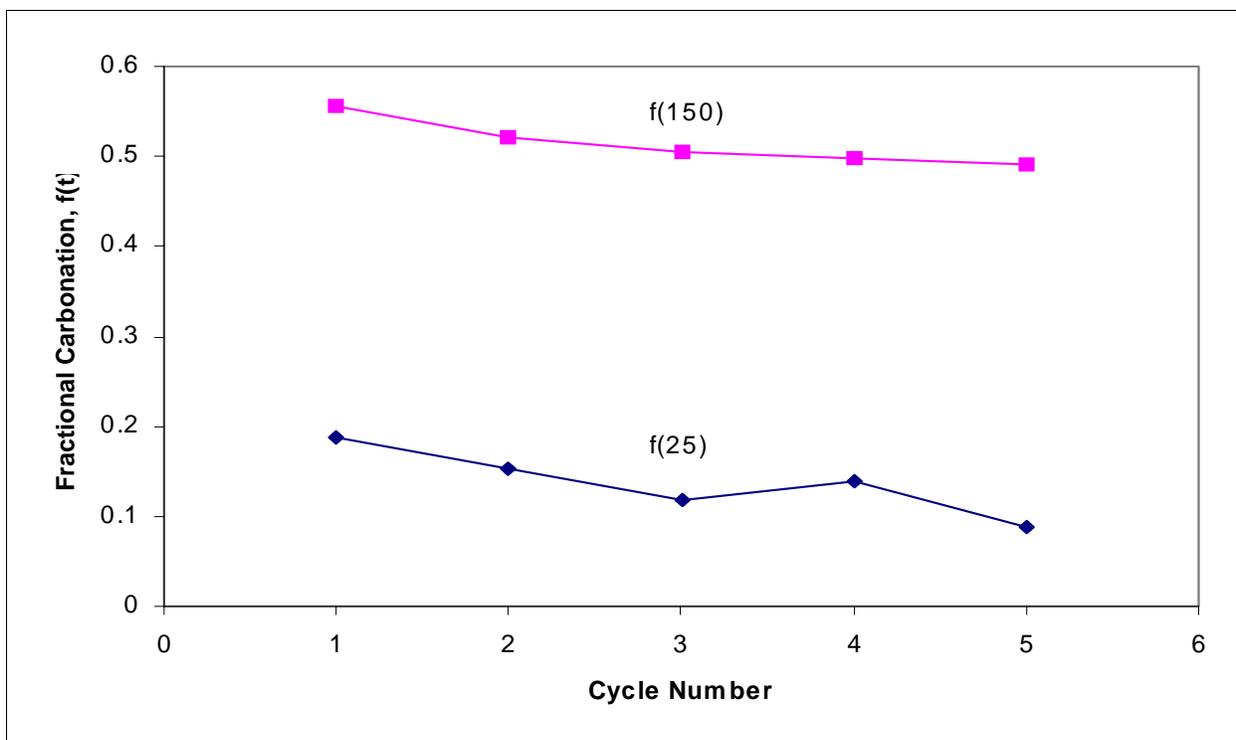


Figure 4. Fractional conversion in 5-cycle test with SBC Grade #3 sorbent (calcination at 200°C in pure CO₂).

Reproducibility of test results under "identical" reaction conditions is shown in Figure 5 where $f(25)$ and $f(150)$ are plotted versus cycle number. Three different samples of SBC Grade #3 were subjected to five complete cycles under standard reaction conditions. Results from the individual runs (91, 92, and 93) are represented by the discrete points while the lines are drawn through the average values of the three tests with the error bars representing "standard deviations. It is obvious that a great deal of scatter exists between the runs, particularly with respect to $f(25)$. In addition, there is no consistent trend as the largest single value of $f(25)$ occurred in Cycle 4 of Test 93. The line representing the average is actually quite similar to the $f(25)$ line from Figure 4. The $f(150)$ results show less scatter and the general trend is also similar to that shown in Figure 4. The average value of $f(150)$ in Cycle 5 is 23% less than the average $f(150)$ value in Cycle 1.

Similar reproducibility results for two duplicate tests using SBC Grade #3 with calcination at 200°C in pure CO₂ are shown in Figure 6. It is immediately evident that there is less overall scatter than shown previously, but the overall trends are similar. Although $f(150)$ decreases with increasing cycle number, the average value of $f(150)$ in Cycle 5 is only 15% less than the Cycle 1 value. The average value of $f(25)$ in Cycle 5 is 46% lower than the Cycle 1 value. Also, the $f(25)$ values do not show a consistent decrease as indicated by the Run 94 (calcination at 200°C in pure carbon dioxide) results in Cycles 2 and 3 (see Figure 6).

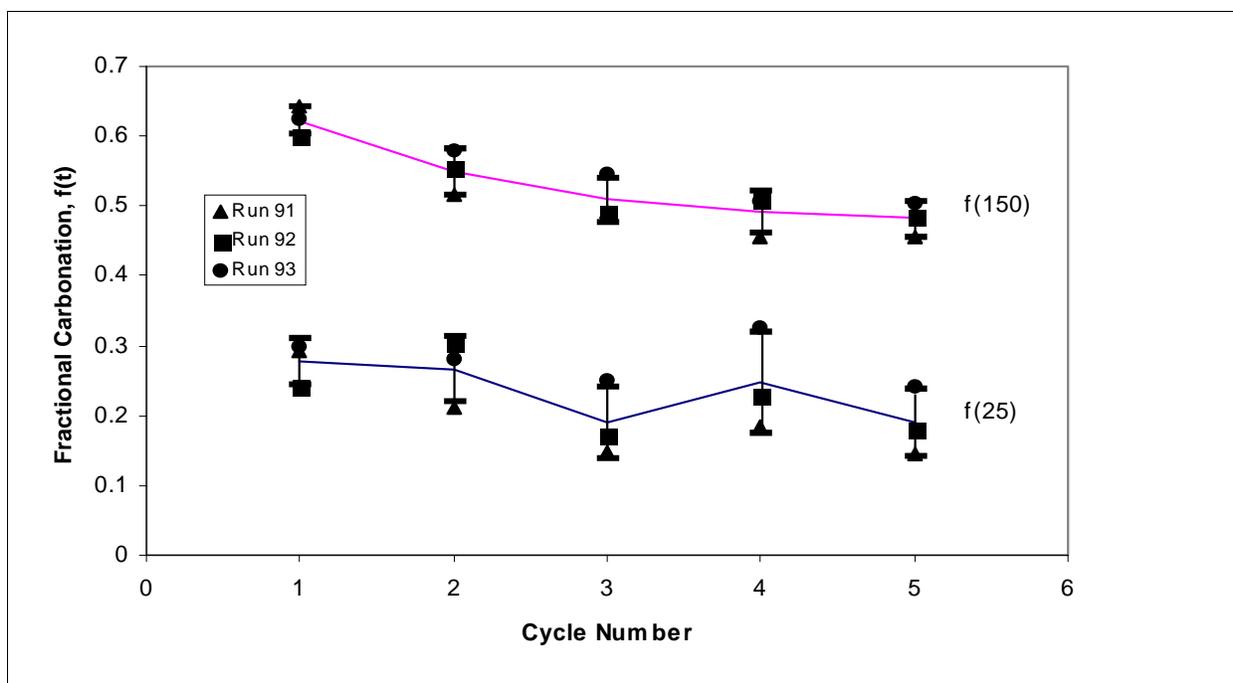


Figure 5. Fractional conversion results from triplicate tests with SBC Grade #3 (calcination at 120°C in pure He).

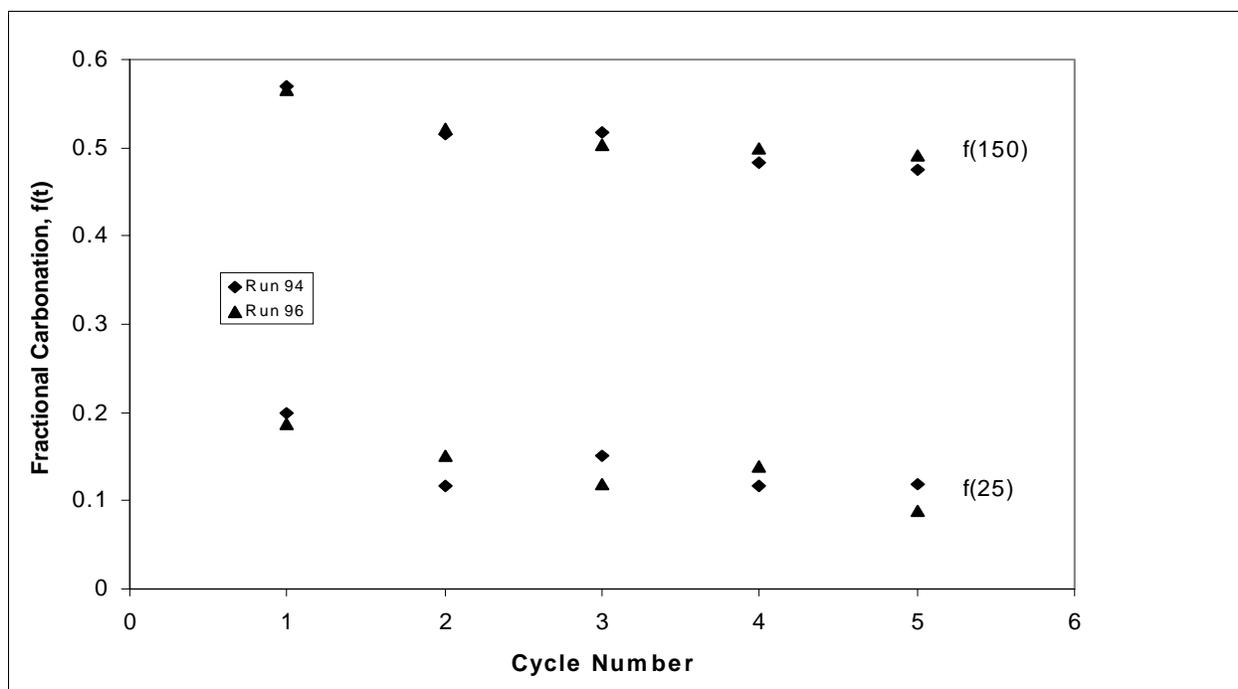


Figure 6. Fractional conversion results from two duplicate tests with SBC Grade #3 (calcination at 200°C in pure CO₂).

At one point, there was some concern that the overall duration of the 5-cycle test would have an effect on performance. In Test 94, the first calcination and carbonation were carried out during Day 1, Cycles 2 and 3 were carried out the second day, and then Cycles 4 and 5 during the third day. In Test 96 (see Figure 6), the five cycles were carried out in five consecutive days. In all cases the carbonated sorbents were left overnight at 70°C in CO₂. However the data from Figure 6 suggest that this concern was unfounded.

Results from the three different calcination conditions are compared in Figure 7. Average values of $f(25)$ and $f(150)$ are plotted for the three runs using calcination in He at 120°C and the two runs using calcination in CO₂ at 200°C. Only a single five-cycle run using calcination in 80%CO₂/20%H₂O at 200°C was completed. Calcination in He at 120°C resulted in the largest values of $f(150)$ during Cycles 1 and 2, but $f(150)$ values for all three conditions were quite similar during Cycles 3, 4, and 5. The $f(25)$ values for calcination in He at 120°C were larger throughout the five cycles.

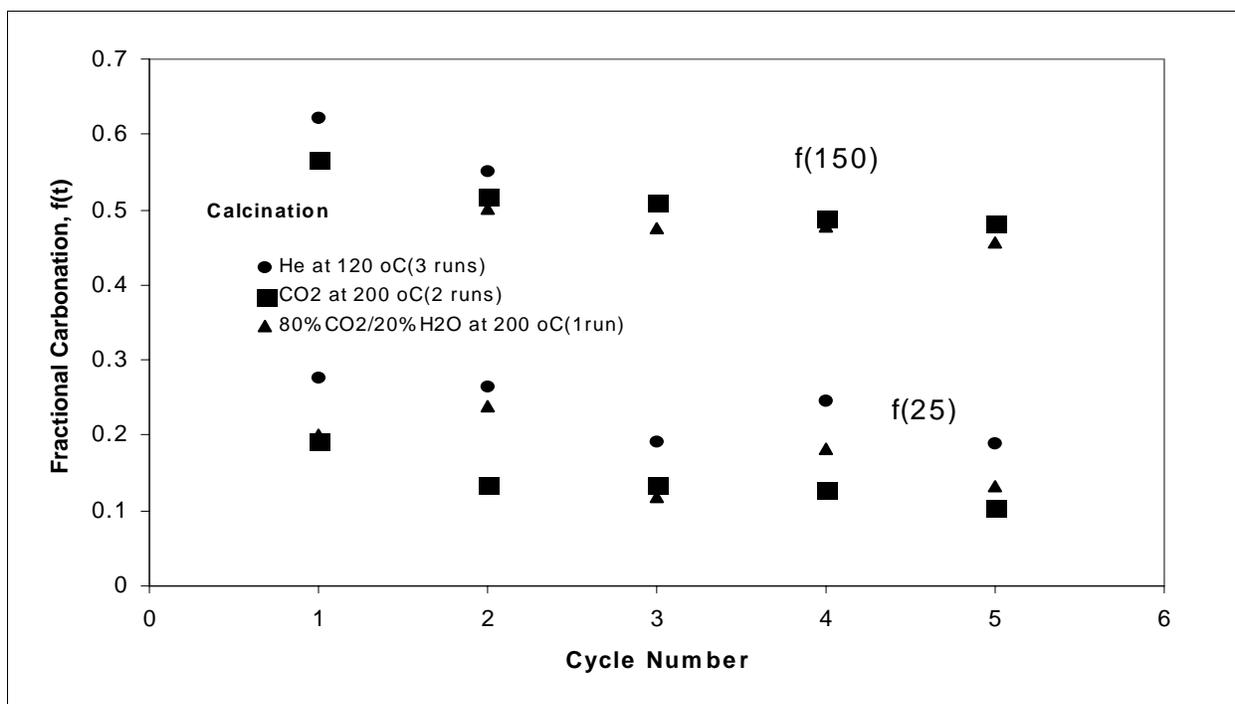


Figure 7. Comparison of $f(25)$ and $f(150)$ results for three different calcination conditions.

4.2 Fixed Bed Reactor Tests at LSU.

Minor modifications to the LSU fixed bed reactor system were made in preparation for one preliminary test conducted this quarter. Results of this test, in terms of mol percent CO₂ in the product gas (dry basis) as a function of time are shown in Figure 8. Approximately 20 g of SBC Grade #3 was loaded into the reactor. This sample was first calcined in He at 120°C and

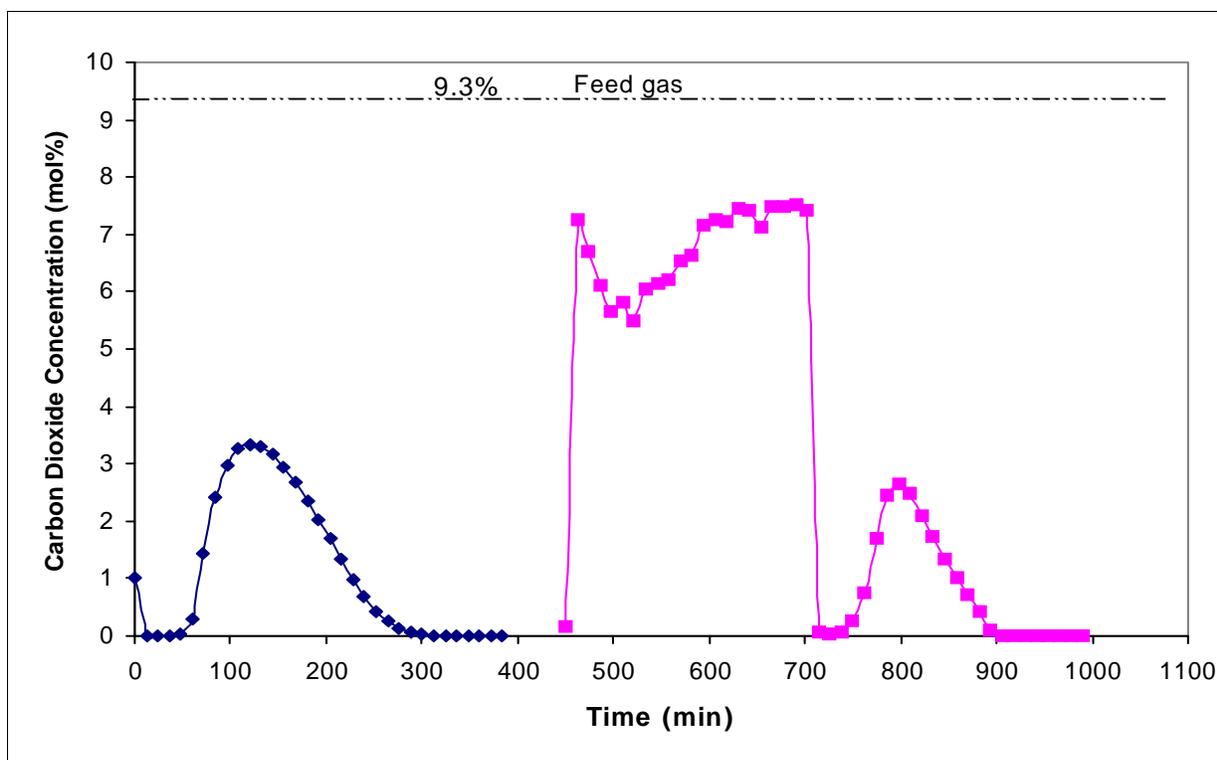


Figure 8. CO₂ concentration in fixed bed reactor product gas stream.

then carbonated in 8% CO₂, 16% H₂O, balance He at 70°C at 600 scc/min (standard calcination and carbonation conditions). A second calcination then followed. The first peak in Figure 8 represents CO₂ produced during the initial calcination, which was continued until no more CO₂ was detected in the product gas. The 20 g of NaHCO₃ should, upon complete calcination, produce 0.119 mol of CO₂. However, numerical integration under the CO₂-time curve accounted for only 0.09 mol of CO₂, an error of 24%. This error is most likely due to an incorrectly calibrated He flow meter.

Following this initial calcination, the sample was then allowed to cool overnight in the reactor to 70°C. The carbonation cycle was initiated the next morning. An initial spike in CO₂ concentration at 7.3% followed by a decrease to 5.6% and a second increase to a final value of 7.5% (all dry basis) were observed in the outlet gas from the carbonation cycle. The initial spike, which was unexpected, is attributed to the probability that water vapor reached the reactor several minutes after CO₂ and He. Without steam in the reacting gas no carbonation is possible. The final value of 7.5% CO₂ is 19% less than the 9.3% dry basis expected with no CO₂ removal due to reaction. The lower than expected final CO₂ concentration is also attributed to an incorrectly calibrated He flow meter. Once steady-state CO₂ concentration was achieved, the CO₂ and H₂O flows were stopped and temperature was increased to 120°C for the second calcination cycle. Integration under the outlet gas concentration curve for this cycle indicated that 0.44 mols of CO₂ were released, or 49% of the amount produced during the first calcination cycle. This percentage is reasonably consistent with first-cycle fractional carbonation values reported earlier, which were generally in the mid-50% range.

To correct for the inaccuracy in the flow meter, it was assumed that the actual He feed rate was 32% greater than the intended flow rate of 456 scc/min. Under this assumption, the CO₂ produced during the first calcination (calculated by integration under the CO₂-time curve) was 0.119 mols, equal to the theoretical value. The mol percent CO₂ (dry basis) in the feed gas would then have been 7.4%, which is quite close to the measured value of 7.5%, and the overall material balance would close quite well

4.3 Fluidized Bed Testing at RTI

A two cycle calcination/carbonation test was conducted in a fluidized bed reactor. Trona T-50 was added to the reactor to a height of 6 in, resulting in an initial height to diameter ratio of 3. The trona was calcined to sodium carbonate by heating to approximately 120°C in flowing nitrogen for two hours. Nitrogen flow was maintained until the first carbonation test was started. Temperatures for the first carbonation cycle, as shown in Figure 9, averaged 80°C, which was higher than optimal, and resulted from preheating the reactor to too high a temperature before beginning the carbonation phase. Carbon dioxide removal, as shown in Figure 10, declined from about 20% to about 8% during a three hour test. The total mass of carbon dioxide removed was 29.9 grams. The theoretical capacity of the bed based on a sodium bicarbonate endpoint was 103 g. The sorbent was then calcined in the reactor in the same manner that it was before the first cycle.

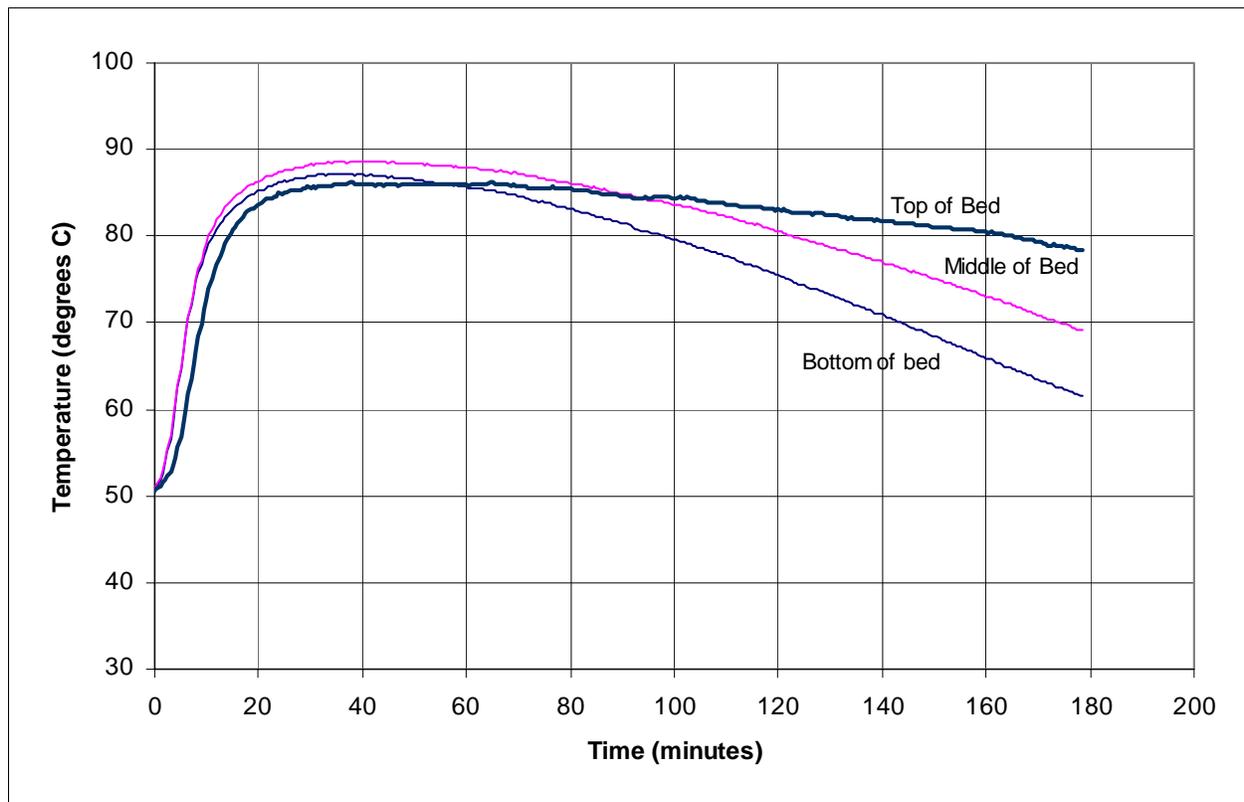


Figure 9. Temperature Profile—Cycle 1 with Trona T-50

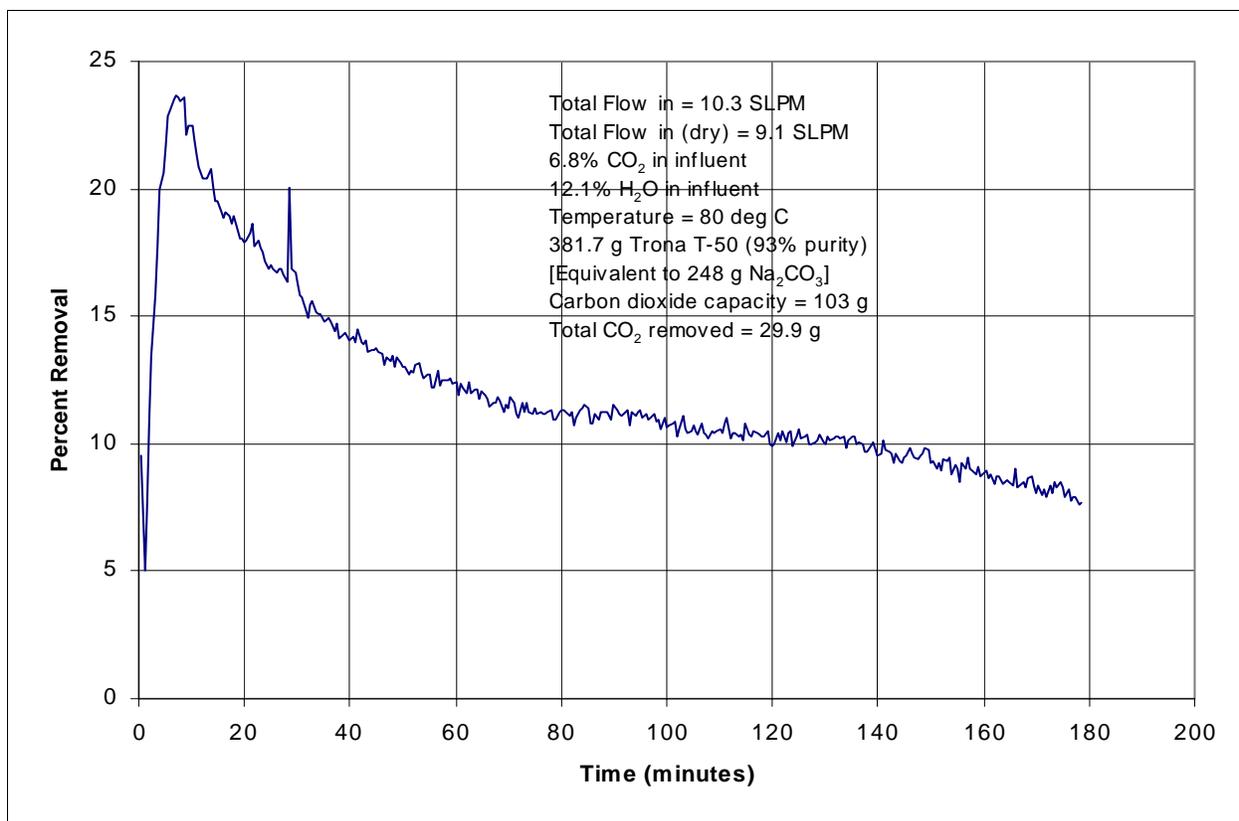


Figure 10. Cycle 1 carbonation test with Trona T-50.

The second carbonation cycle was conducted at a lower, theoretically more favorable temperature, averaging 65°C. Bed temperature profiles are shown in Figure 11. Because of the lower feed gas temperature, the water vapor content of the simulated flue gas was decreased from 12.1% to 5.8% for the second cycle to avoid condensing water. Carbon dioxide removal for this cycle, as shown in Figure 12, declined from 11% to 1% over the course of the 160 minutes.

The total mass of carbon dioxide removed was 17.4 g. The theoretical capacity of the bed based on a sodium bicarbonate endpoint was, 103 g, same as before. The decline in activity in the second cycle may have been due to the lower water vapor content available for reaction, or a decline in the activity of the sorbent material.

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. A summary of test results is given in Table 2.

Table 2. Summary of 2 Cycle Carbonation Test Data

Cycle	1	2
Total Flow (SLPM)	10.3	10.9
Dry Flow (SLPM)	9.1	10.3
CO ₂ in (dry %)	6.8	6.7
H ₂ O in (%)	12.1	5.8
Temperature (°C)	80	65
CO ₂ removed (g)	29.9	17.4
Sorbent Capacity Utilization (%)	29.0	16.5

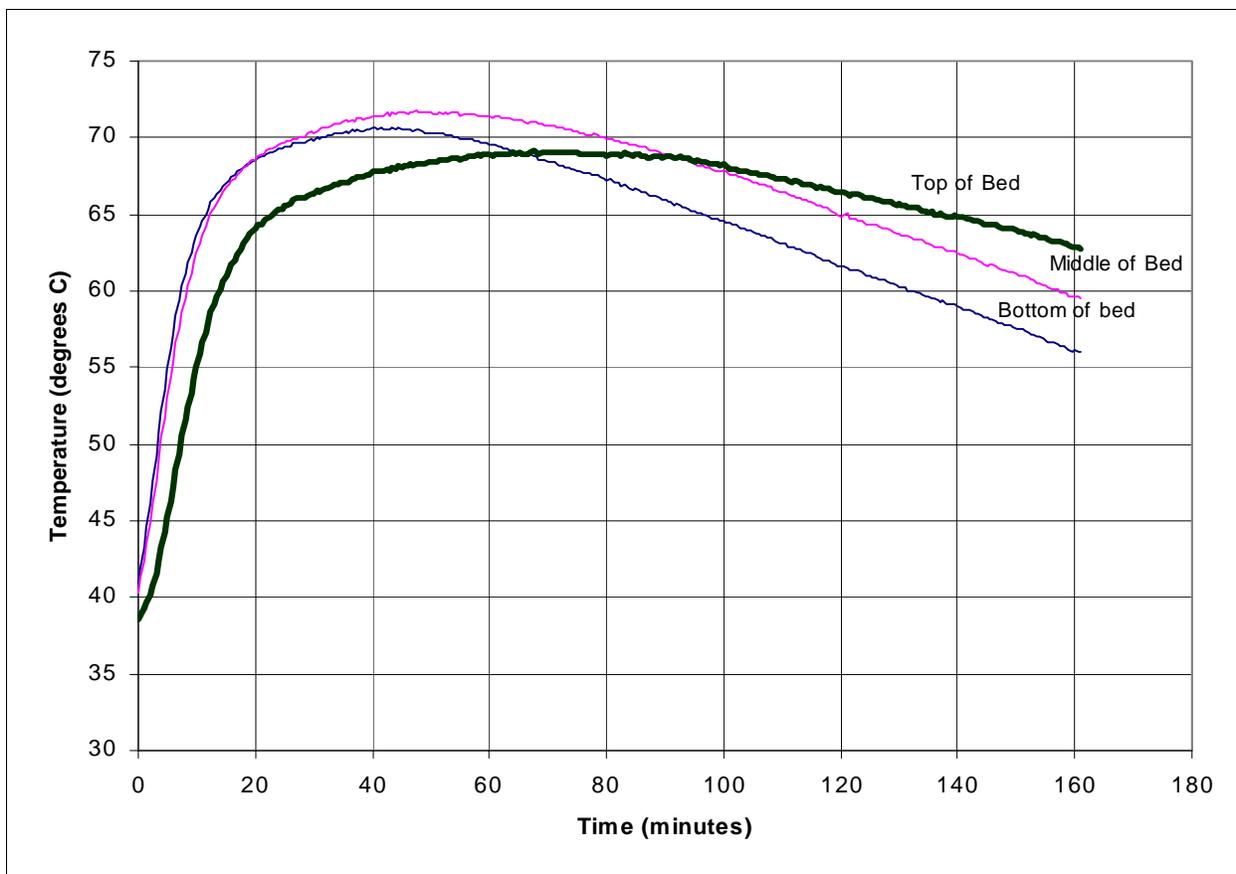


Figure 11. Temperature profile—Cycle 2 with Trona T-50

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.

4.4 Thermodynamic Analysis of Sodium Carbonate Phases

In the July 2001 Quarterly Report (Green et al., 2001c), RTI proposed a mechanism by which kinetic data for the carbonization of sodium carbonate obtained in TGA experiments could be explained in terms of the transfer of the reaction heat from reacting particle to the bulk gas. In brief, based on theoretical arguments, it was proposed that the initial reaction rate of sodium carbonate with steam and carbon dioxide would be proportional to the difference between the equilibrium temperature for the carbonization reaction, evaluated at the bulk gas composition, and the bulk gas temperature. Thus

$$\text{Rate}_{\text{initial}} = \left. \frac{dx}{dt} \right|_{t=0} = h'(T_{\text{eq}} - T_b) \quad (4)$$

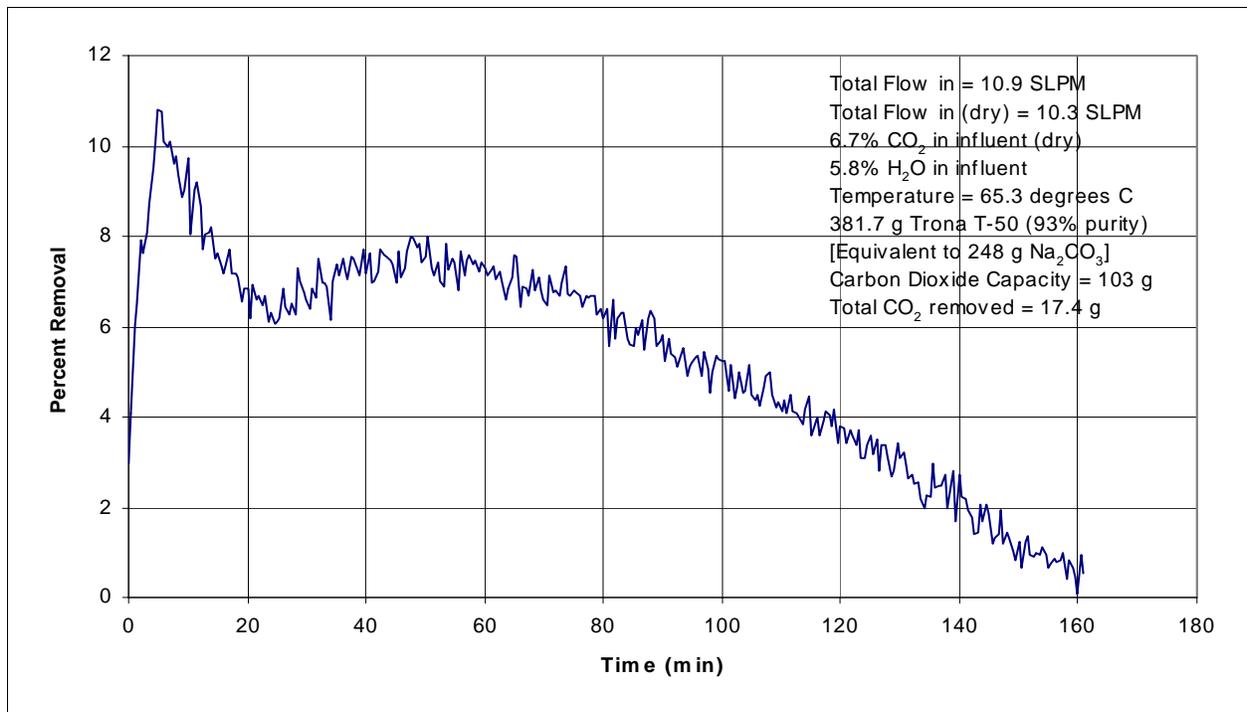


Figure 12. Cycle 2 carbonation test with Trona T-50.

where x is the conversion of sodium carbonate

t is the time, sec

h' is a proportionality constant, $(K \text{ sec})^{-1}$

T_{eq} is the equilibrium temperature determined by thermodynamics at the bulk gas composition, K

and T_b is the bulk gas temperature, K

Equation (4) was derived based on the observations that the carbonization of sodium carbonate is highly exothermic being approximately 30 kcal/gmol CO₂ reacted and thus the thermodynamic favorability of the carbonization reaction decreases with increase in temperature until the reaction stops at the equilibrium temperature, T_{eq} . Also, it was observed in the July 2001 Quarterly Report (Green et al., 2001) that a small change in CO₂ concentration between the bulk phase and that at the reacting surface would give rise to a large temperature difference between the reacting surface and the bulk gas, thus it was argued that the driving force for heat transfer from the particle would be approximately the difference between the equilibrium temperature evaluated at bulk concentration and the bulk temperature.

Based on the theory sent forth above and represented by Equation (4), the proportionality constant, h' , is a function of the heat transfer coefficient, the total heat of reaction that could be released by the complete carbonization of the sodium carbonate within the particle and the external surface area of the particle. Thus

$$h' = \frac{hA_p}{N_o(-\Delta H)} \quad (5)$$

where h is the heat transfer coefficient between the external surface of the particle and the bulk gas, cal/(sec cm² K)
 A_p is the external area of the particle, cm²
 N_o is the initial moles of Ca₂CO₃ in the particle, gmol
 and ΔH is the heat of reaction for the carbonization of the Na₂CO₃, cal/gmol Na₂CO₃

The factors comprising h' are expected to be weak functions of temperature, yet when h' was calculated for the limited TGA data available, the activation energy for h' was 14.4 kcal/gmol. This observation was explained by hypothesis that a systematic error in the analysis had been made.

The systematic error was the assumption that sodium carbonate was for being carbonized to form sodium bicarbonate (NaHCO₃) when in fact the product being formed for most of the TGA data reported in the July Quarterly Report (Green et al., 2001c) appears to be, Na₂CO₃•3NaHCO₃. Examination of the figures in the July 2001 Quarterly Report reporting the carbonization of sodium carbonate at temperatures of 70°C and 80°C shows that most of the dimensionless weight gain curves asymptotically approach a dimensionless weight of approximately 0.85. This is exactly the value that would be approached if the carbonization product was Na₂CO₃•3NaHCO₃. An example of the TGA weight gain curves reported in the July 2001 Quarterly Report (Green et al., 2001) as Figure 11 is reproduced in this Quarterly Report as Figure 13.

As can be seen in Figure 13, the dimensionless weight curve for the carbonization of sodium carbonate (at a bulk gas temperature of 70°C) levels off at a value 0.85 indicating that the final product could perhaps be Na₂CO₃•3NaHCO₃. The curve at 60°C shows a dimensionless weight gain in excess of 0.85 indicating that some of the reaction product must contain NaHCO₃. In the discussion below, it will be shown that the initial reaction rate for the 60°C curve is consistent with the formation of Na₂CO₃•3NaHCO₃.

The reaction of the particle with CO₂ and steam can be viewed as follows. Initially, at the surface, the reaction begins and the particle surface quickly rises to approximately the limiting equilibrium temperature due to the extreme exothermic nature of the carbonization reaction. At this temperature Na₂CO₃•3NaHCO₃ forms. As the reaction front proceeds into the particle, the particle surface begins to cool due to the low bulk gas temperature. As the surface temperature reaches the equilibrium temperature for the bicarbonate formation, sodium bicarbonate forms and continues to form as the outer portion of the particle cools below the bicarbonate equilibrium temperature. Thus based on this picture of the dimensionless weight curves, NaHCO₃ is the more favored product of Na₂CO₃ carbonization at lower temperatures and Na₂CO₃•3NaHCO₃ is the favored product at higher temperatures.

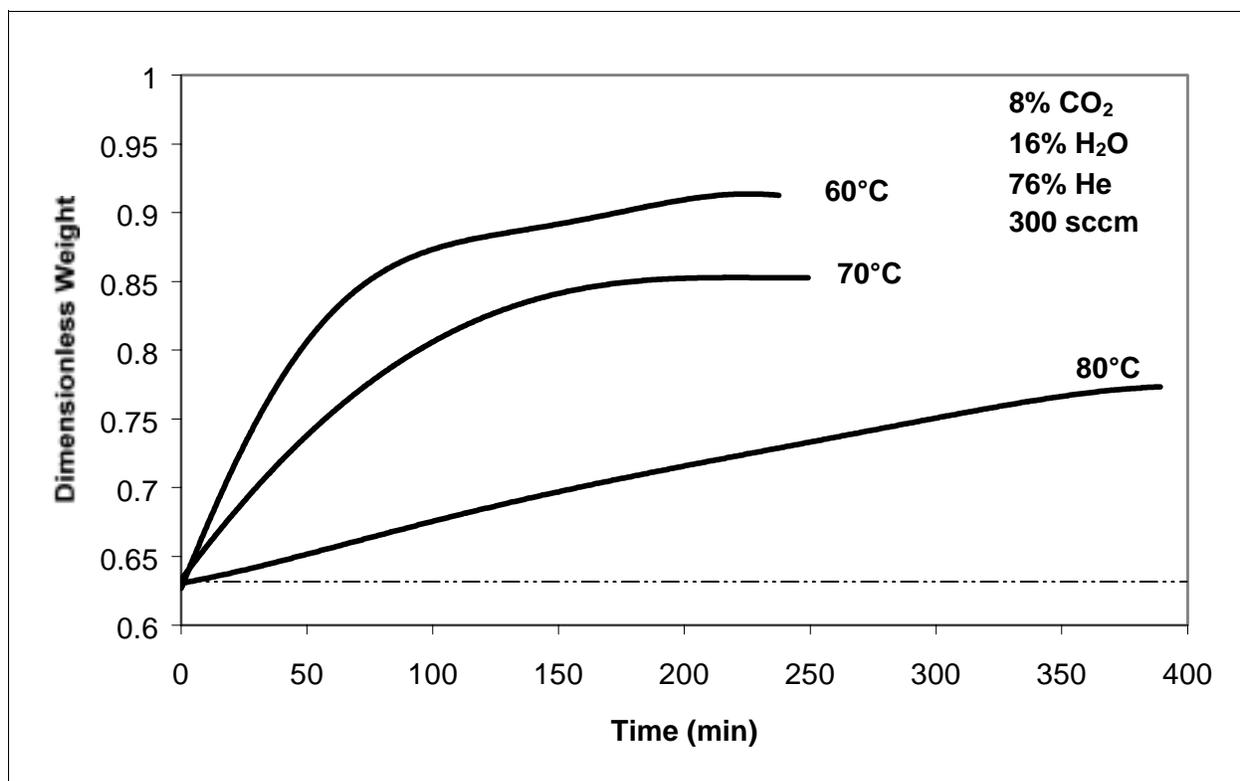
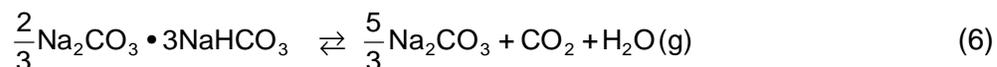


Figure 13. Effect of carbonation temperature using SBC grade #3.

Unfortunately, the above described order of stability is not that predicted by the widely used HSC Chemistry Thermodynamics Program. The HSC Chemistry equilibrium data for the carbonization reaction



for temperatures between 60°C and 100°C can be correlated by the following expression

$$\ln K_1 = 41.863 - 16518 / T(\text{K}) \quad (7)$$

where

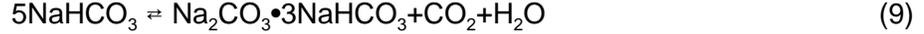
$$K_1 = P_{\text{CO}_2} P_{\text{H}_2\text{O}} \quad (8)$$

K_1 is the equilibrium constant for Reaction (6), atm.²

P_{CO_2} , $P_{\text{H}_2\text{O}}$ are the partial pressures of CO_2 and H_2O , respectively, atm.

and T is the absolute temperature, K.

Further carbonization of $\text{Na}_2\text{CO}_3 \cdot 3\text{NaHCO}_3$ to NaHCO_3 is given by the following reaction



The HSC Chemistry equilibrium data for this reaction of temperatures between 60°C and 100°C can be approximated by

$$\ln K_2 = 39.538 - 16175 / T(\text{K}) \quad (10)$$

$$K_2 = P_{\text{CO}_2} P_{\text{H}_2\text{O}} \quad (11)$$

where K_2 is the equilibrium constant for Reaction (9), atm^2 .

To illustrate the order of thermal stability predicted by the HSC Chemistry for the various sodium carbonates involved in producing NaHCO_3 by the carbonation of Na_2CO_3 , Equations 7 and 10 can be plotted as shown in Figure 14. Assuming that Le Chatelier's principle holds for the Reactions (6) and (9), then the area above the equilibrium line for Reaction (6) should be an area where the formation of $\text{Na}_2\text{CO}_3 \cdot 3\text{NaHCO}_3$ is favored and the area below the equilibrium line for Reaction (9) is an area where conditions would dictate that $\text{Na}_2\text{CO}_3 \cdot 3\text{NaHCO}_3$ is also formed. Thus, according to HSC Chemistry, it would be possible to expose $\text{Na}_2\text{CO}_3 \cdot 3\text{NaHCO}_3$ to an atmosphere containing CO_2 and H_2O (where $P_{\text{CO}_2} \cdot P_{\text{H}_2\text{O}}$ had a low numerical value) and, by increasing the CO_2 partial pressure at constant $P_{\text{H}_2\text{O}}$ and temperature produce NaHCO_3 . Then, upon further increase in CO_2 partial pressure Na_2CO_3 would be produced in violation of Le Chatelier's principle. Further increase in CO_2 pressure would again eventually produce $\text{Na}_2\text{CO}_3 \cdot 3\text{NaHCO}_3$. It is clear that the HSC Chemistry data are misleading, and that the equilibrium line for Reaction (9) should be above the equilibrium line for Reaction (6). Thus, $\text{Na}_2\text{CO}_3 \cdot 3\text{NaHCO}_3$ should be more thermally stable than NaHCO_3 as suggested by the LSU TGA data (an example of which is shown in Figure 13.)

Church and Dwight has supplied RTI with phase diagrams for the Na_2CO_3 , NaHCO_3 , and $\text{Na}_2\text{CO}_3 \cdot 3\text{NaHCO}_3$, CO_2 and water vapor system. An example of this phase diagram for a relative humidity (RH) of 40% is shown in Figure 15. From this figure, it appears that the $\text{Na}_2\text{CO}_3 \cdot 3\text{NaHCO}_3$ is more thermally stable than NaHCO_3 which is in agreement with the TGA data but opposite the thermal stability order predicted by the HSC Chemistry. Church and Dwight supplied a sequence of phase diagram such as that shown in Figure 15 for relative humidities (RH) of 100%, 80%, 60%, 40%, 20% and 5%. The data in the phase diagram for 60, 40, 20 and 5% RH were replotted as the product of the CO_2 and H_2O partial pressures as a function temperature as shown in Figure 16. Phase diagrams for 80 and 100% RH were not used due to distortions in the equilibrium curves for $\text{Na}_2\text{CO}_3 \cdot 3\text{NaHCO}_3$ and NaHCO_3 introduced by the presence of other chemically distinct sodium carbonates occurring at the temperatures of interest which ranged from 60 to 100°C.

The equilibrium data calculated using HSC Chemistry and the data of Church and Dwight, are compared in Figure 17. Figure 17 shows clearly the discrepancy in the order of thermal stability of NaHCO_3 and $\text{Na}_2\text{CO}_3 \cdot 3\text{NaHCO}_3$ between the work of Church and Dwight, and HSC Chemistry.

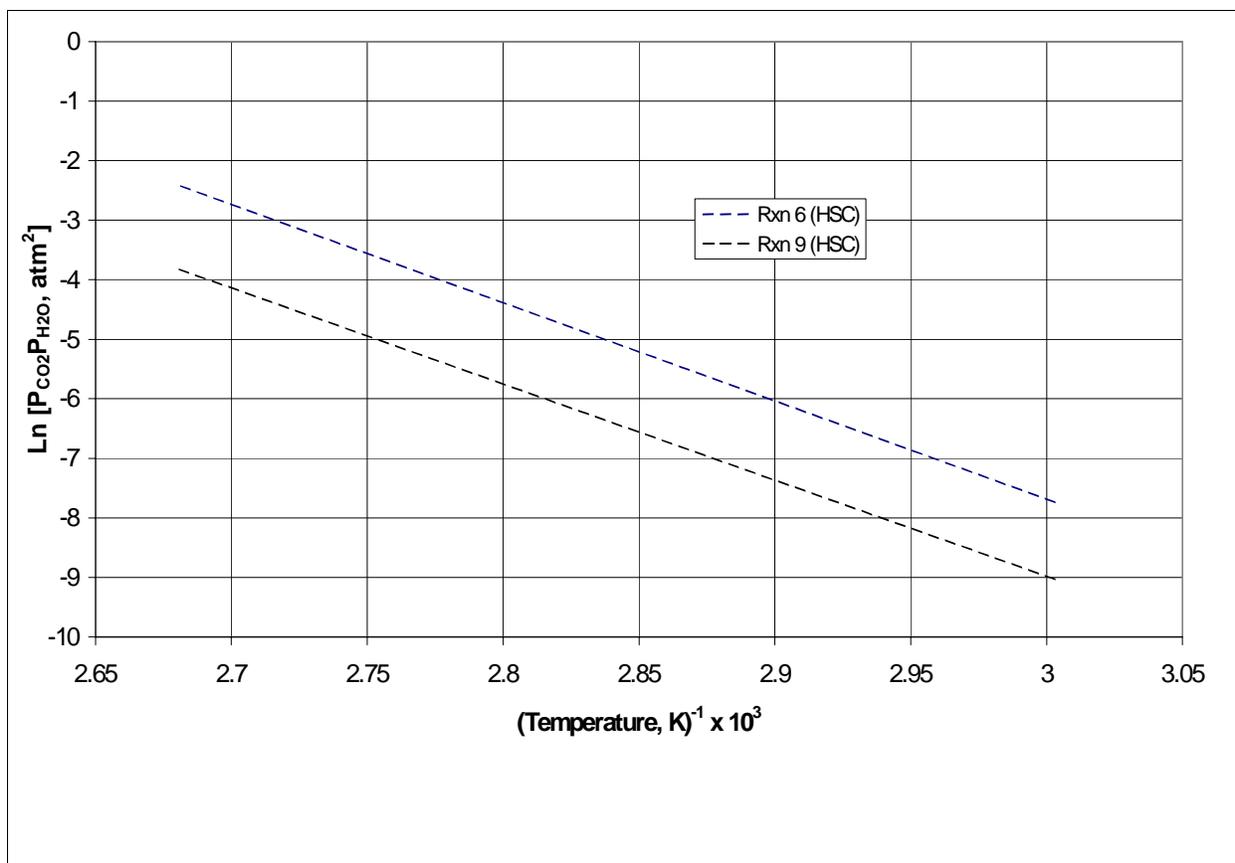


Figure 14. Equilibrium curves for a sodium carbonate-sodium bicarbonate system generated using the HSC chemistry software.

For reference, the Church and Dwight equilibrium data for $\text{Na}_2\text{CO}_3 \cdot 3\text{NaHCO}_3$ formation via Reaction (6) shown in Figures 16 and 17 can be represented by

$$\ln K_1 = 36.256 - 15187 / T \quad (12)$$

and the equilibrium data for NaHCO_3 formation via Reaction (9) is given by

$$\ln K_2 = 37.792 - 14658 / T \quad (13)$$

The equilibrium data of Church and Dwight as represented by Figures 15, 16 and 17 date to 1977 or earlier.

To resolve the discrepancies between the equilibrium data of Church and Dwight, and that produced by HSC Chemistry, other sources of thermodynamic data for the chemical species involved in Reactions (6) and (9) are needed. One source that RTI has used is older data on enthalpy and free energy of formation and heat capacity from Perry's Chemical Engineering Handbook (Perry et al., 1963). Using these data and estimating the heat capacity of Na_2CO_3

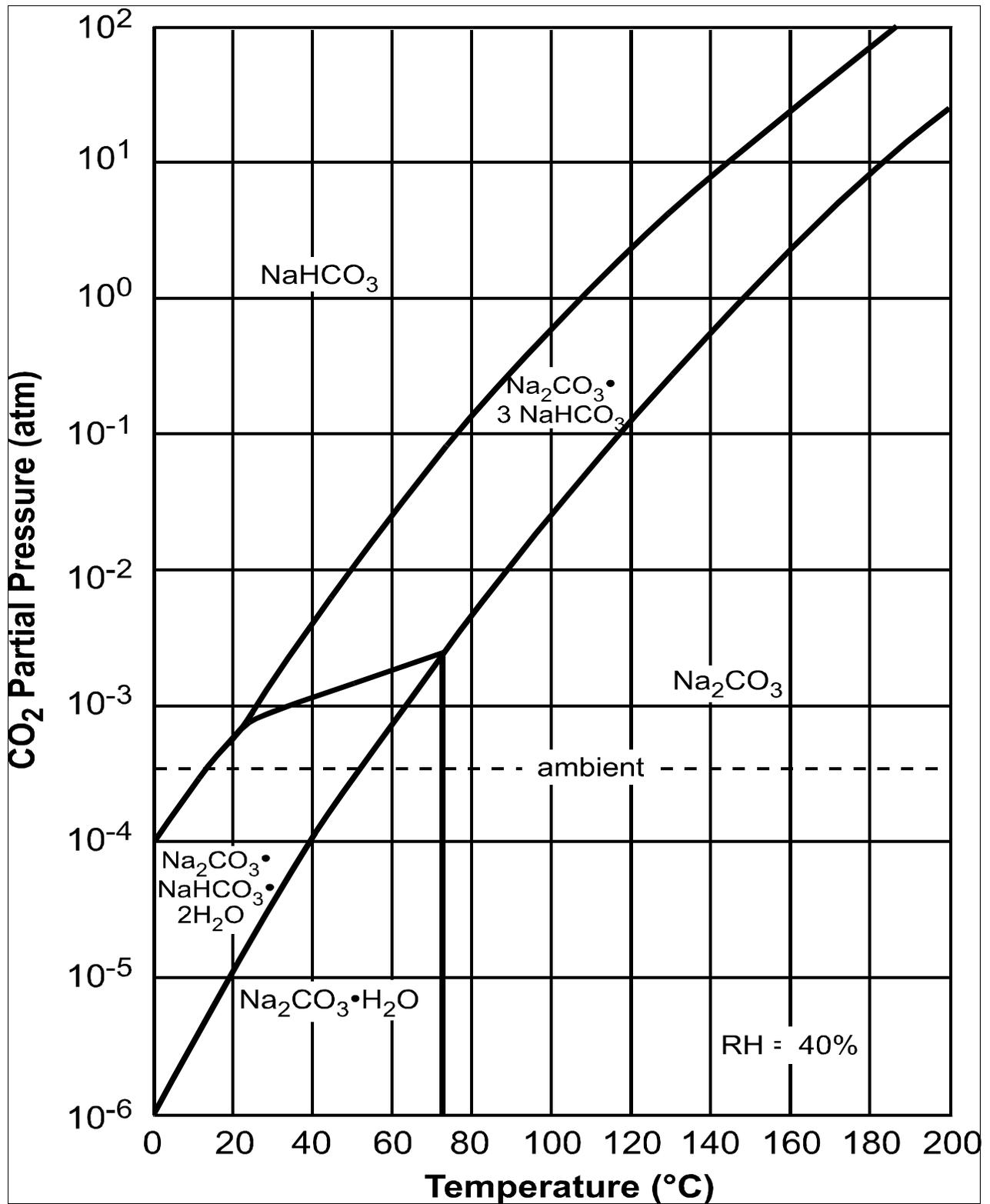


Figure 15. Phase diagram for sodium carbonate/sodium bicarbonate system. (Source: Church and Dwight)

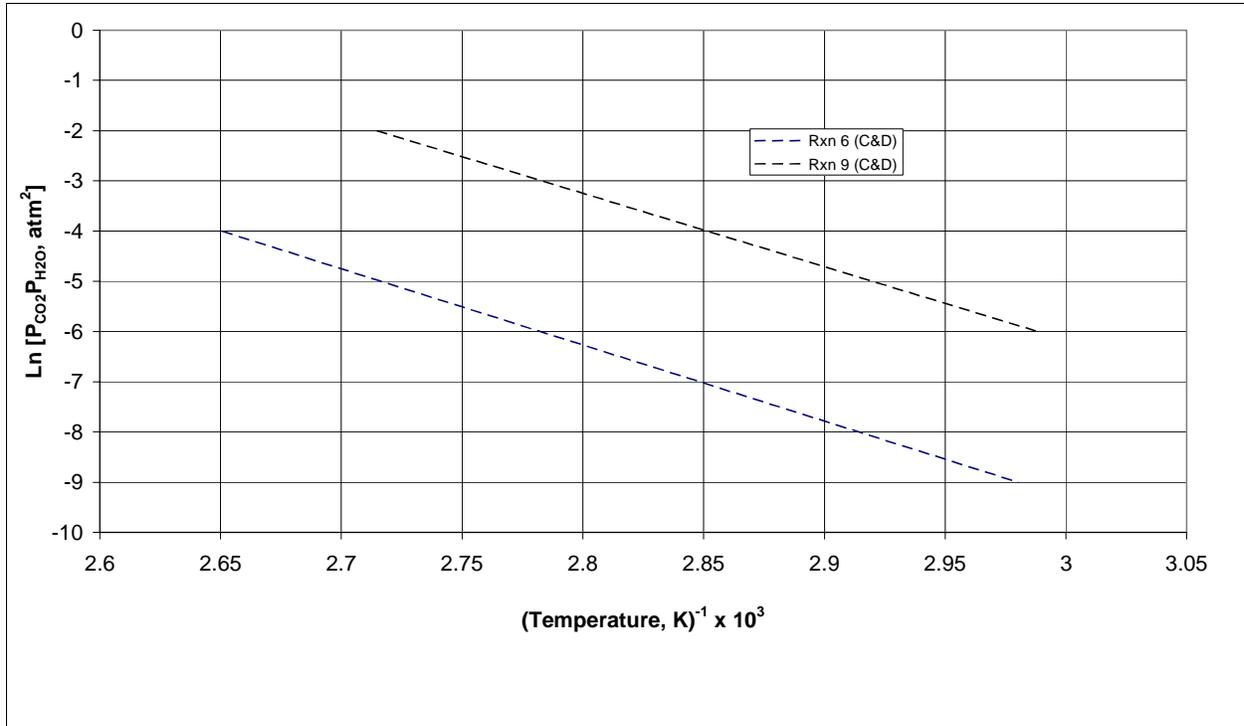


Figure 16. Equilibrium constants for the sodium carbonate - sodium bicarbonate system using data obtained from Church and Dwight

and NaHCO_3 by the method of Lewis and Randall (1923), the equilibrium constant for the following reaction



can be found. According to the phase diagrams of Church and Dwight (see Figure 15), equilibrium between the Na_2CO_3 and NaHCO_3 phases does not exist and at equilibrium, $\text{Na}_2\text{CO}_3 \cdot 3\text{NaHCO}_3$ intervenes between these two phases. Therefore the equilibrium of Reaction (14) can be viewed as hypothetical. Using the thermodynamic data of Perry's Handbook and heat capacity estimation methods of Lewis and Randall (1923), the equilibrium constant for Reaction (14) between the temperatures of 65 and 105°C can be represented as

$$\ln K_3 = 40.356 - 15490 / T \quad (15)$$

$$K_3 = P_{\text{CO}_2} P_{\text{H}_2\text{O}} \quad (16)$$

where K_3 is the equilibrium constant for Reaction (14), atm^2 .

The free energy and enthalpy of formation for the formation of $\text{Na}_2\text{CO}_3 \cdot 3\text{NaHCO}_3$ were not available from Perry's Chemical Engineering Handbook (1963).

The equilibrium data for Reaction (14) derived from the information from Perry's Handbook and summarized by Equation 15 is shown in Figure 17. As can be seen from this figure, agreement

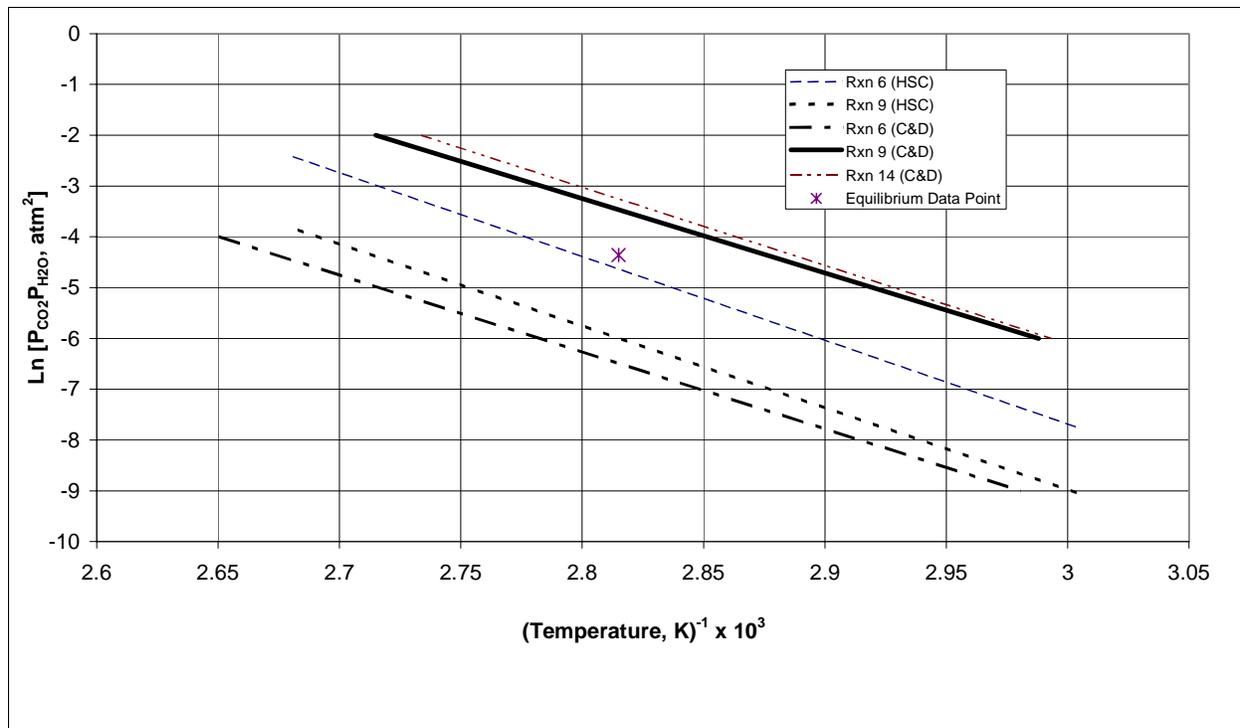


Figure 17. Comparison of equilibrium constants for reactions 6, 9, & 14.

between the equilibrium constant, K_2 , for Reaction (9) derived from Church and Dwight phase diagrams and the equilibrium constant, K_3 , for Reaction (14) derived from Perry's Handbook is fairly close but not exact. The degree to which these equilibrium constants agree and the age of the thermodynamic data from Perry's raises the question that, in the possible absence of the knowledge of the compound $\text{Na}_2\text{CO}_3 \cdot 3\text{NaHCO}_3$, the thermodynamic data in Perry's Handbook for Reaction (14) may have been derived from knowledge of the CO_2 decomposition pressure of NaHCO_3 . Considering the existence of $\text{Na}_2\text{CO}_3 \cdot 3\text{NaHCO}_3$ and the phase diagrams of Church and Dwight, it is possible that the decomposition pressure of NaHCO_3 could be that given for the equilibrium of Reaction (9). Therefore, the equilibrium constant, K_2 , derived from the data of Church and Dwight and the equilibrium constant K_3 derived from the data of Perry's Handbook could represent the same thing; that is the decomposition of NaHCO_3 to $\text{Na}_2\text{CO}_3 \cdot 3\text{NaHCO}_3$ (Reaction 9). Therefore, under the scenario described above, the agreement of the equilibrium constants should not be unexpected. Due to this fairly good agreement, the equilibrium constant for Reaction (9) is probably close to the equilibria described by Equation (13) or Equation (15). Little faith can be placed in the equilibrium constant, K_2 , calculated by HSC Chemistry. Further research is needed to clarify when and under what conditions different carbonate phases are formed. This is critical to the understanding of the reaction kinetics of the carbonization of Na_2CO_3 .

The TGA kinetic data obtained by LSU, such as that illustrated in Figure 13, can be shown to be consistent with the kinetic rate expression given by Equation (4) and the hypothesis that at the initial stage of reaction, $\text{Na}_2\text{CO}_3 \cdot 3\text{NaHCO}_3$ is the primary reaction product.

In the July 2001 Quarterly Report, it was shown that the initial rate data from the LSU TGA kinetic experiments could be well correlated at low conversion by the expression

$$-\ln(1-x) = kt \quad (17)$$

where k is a rate constant which is precisely equal to the initial rate of reaction. Thus applying Equation (4) to Equation (17) yields

$$\left. \frac{dx}{dt} \right|_{t=0} = k = h'(T_{eq} - T_b) \quad (18)$$

Why the initial rate data from the TGA experiments would follow the logarithmic expression given by Equation (17) rather than some other expression has not been fully resolved at this time; however, Equation (17) can represent the initial rate data quite well. Using Equation (17) and assuming the conversion, x , refers to the conversion of Na_2CO_3 to $\text{Na}_2\text{CO}_3 \cdot 3\text{NaHCO}_3$, the initial rates of conversion for the three temperature curves shown in Figure 13 have been determined and are shown in the second column of Table 3. The least squares fit of these data in the form given by Equation (18) yields

$$h' = 1.83 \times 10^{-5} (\text{sec } ^\circ\text{C})^{-1} \quad (19)$$

$$T_{eq} = 82.2 \text{ } ^\circ\text{C} \quad (20)$$

TABLE 3. Comparison of the Experiment and Computed Initial Conversion Rates of Na_2CO_3 to $\text{Na}_2\text{CO}_3 \cdot 3\text{NaHCO}_3$

T_b , bulk gas temperature, $^\circ\text{C}$	Experimental $\left. \frac{dx}{dt} \right _{t=0}$ Initial Conversion rate of Na_2CO_3 to $\text{Na}_2\text{CO}_3 \cdot 3\text{NaHCO}_3$, sec^{-1}	Initial Conversion Rate, sec^{-1} Computed using least square fit of h' and T_{eq} via Equation 12
60	4.10×10^{-4}	4.07×10^{-4}
70	2.20×10^{-4}	2.24×10^{-4}
80	4.30×10^{-5}	4.03×10^{-5}

In this least squares fit of the data, the heat transfer parameter, h' , has been assumed to be independent of temperature which from its definition would roughly be the case. In the July 2001 Quarterly Report (Green et al., 2001), for the data given in Figure 13 of this present Quarterly Report, the initial conversion rates, k , at 60 to 70 $^\circ\text{C}$ were computed assuming that conversion was based on Na_2CO_3 being converted to NaHCO_3 . Using Equation (17) to calculate h' and assuming T_{eq} could be calculated as 73.4 $^\circ\text{C}$ by Equation (15), the equilibrium curve for the formation of NaHCO_3 from Na_2CO_3 via Reaction (14) yields an activation energy of

roughly 14.4 kcal/gmol for h' (as shown in Figure 13 of the July 2001 Quarterly Report) counter to the fact that the actual activation energy for h' , based on its definition, should be about 0.2 kcal/gmol. As described above the equilibrium constant K_3 determined from the data in Perry's Handbook could be viewed as the equilibrium constant K_2 for the reaction of $\text{Na}_2\text{CO}_3 \cdot 3\text{NaHCO}_3$ to NaHCO_3 . Thus it can be concluded that the equilibrium temperature, T_{eq} , given by Equation (15), the equilibrium curves for the formation of NaHCO_3 from $\text{Na}_2\text{CO}_3 \cdot 3\text{NaHCO}_3$, gives rise to an incorrect driving force for the initial rate of conversion of Na_2CO_3 and cannot explain the TGA data shown in Figure 13.

Returning to Table 3, the result assuming h' independent of temperature and using least squares fit of the data gives $h' = 1.10 \times 10^{-3} (\text{°C min})^{-1}$ and $T_{\text{eq}} = 82.2\text{°C}$. Using these values in Equation 18, the initial conversion rates for the three temperatures in Table 3 have been calculated as shown in the third column of Table 3. Comparing the second and third columns shows that the experimental and calculated initial conversion rates, respectively, are very close and consistent.

If the equilibrium temperature at the surface of the particle is not given by the equilibrium of Reaction (9), (the formation of NaHCO_3 from $\text{Na}_2\text{CO}_3 \cdot 3\text{NaHCO}_3$) as shown above then it is possible that the equilibrium of Reaction (6), (the formation of $\text{Na}_2\text{CO}_3 \cdot 3\text{NaHCO}_3$ from Na_2CO_3) could determine the equilibrium temperature and hence the driving temperature difference which is needed to remove heat from the particle so that the carbonation of Na_2CO_3 may proceed.

The analysis of the TGA data in Figure 13 shows that an equilibrium temperature, T_{eq} , of 82.2°C, explains the data well. Since, as explained above, during the initial portion of the TGA experiment the partial pressure of CO_2 and H_2O will be very close to the respective bulk gas partial pressures, then $\ln[P_{\text{CO}_2} P_{\text{H}_2\text{O}}]$ at the surface will be approximately equal to -4.358 . This logarithm of the partial pressure product has been plotted on Figure 17 at the equilibrium temperature, $T_{\text{eq}} = 82.2\text{°C}$, associated with the TGA data given in Figure 13 derived from the least squares fit of the initial rate data shown in Table 3. As can be seen in Figure 17, this single data point lies close to the equilibrium curve for the formation of $\text{Na}_2\text{CO}_3 \cdot 3\text{NaHCO}_3$ from Na_2CO_3 [Reaction (6)] determined from the equilibrium data produced by HSC Chemistry. The difference between the "equilibrium" data point calculated from the TGA data shown in Figure 13, and the HSC Chemistry equilibrium curve is not much more than the difference between the equilibrium curves for Reaction (9) (the formation of $\text{Na}_2\text{CO}_3 \cdot 3\text{NaHCO}_3$ from Na_2CO_3) as shown in Figure 17 which were produced using thermodynamic data from Perry's Handbook and the phase diagrams of Church and Dwight. Also, the single equilibrium data point shown in Figure 17 calculated from the TGA data might imply that the equilibrium curve derived from HSC Chemistry may be more accurate than the curve derived from the Church and Dwight phase diagrams for Reaction (6).

Using the equilibrium curve [for Reaction (6)] in Figure 17 produced by data from HSC Chemistry would give an equilibrium temperature T_{eq} , of 84.4°C for a gas having $P_{\text{CO}_2} = 0.08$ atm and $P_{\text{H}_2\text{O}} = 0.16$ atm. While $T_{\text{eq}} = 82.2\text{°C}$, computed from the best fit of the TGA data given in Figure 13, is very close to the value of 84.4°C obtained from the curves in Figure 17, the use of this value of T_{eq} , of 84.4°C could introduce significant errors in calculating the rates of carbonization of Na_2CO_3 when operating a reaction at bulk gas temperatures approaching the equilibrium temperature. Since this would not be good practice, using the thermodynamic equilibrium data for Reaction (6) produced by HSC Chemistry could give reasonable estimates

of the carbonization rate at practical operating conditions; i.e., the bulk gas temperature is kept well below the bulk gas equilibrium temperature.

Based on arguments given above, it can be shown from Figure 17 that for the carbonizing gas used in the TGA experiments that are summarized in Figure 13, NaHCO_3 cannot form above 73°C . Therefore the carbonization of Na_2CO_3 at 80°C must involve only the formation of $\text{Na}_2\text{CO}_3 \cdot 3\text{NaHCO}_3$. For the experiment carried out at 70°C it is possible for both NaHCO_3 and $\text{Na}_2\text{CO}_3 \cdot 3\text{NaHCO}_3$ to form; however over the length of the TGA experiment it can be seen from Figure 13 that the dimensionless weight gain curve asymptotically approaches 0.85 which is the value it should approach if $\text{Na}_2\text{CO}_3 \cdot 3\text{NaHCO}_3$ was being formed during the carbonization of Na_2CO_3 . The formation of NaHCO_3 is not observed even though both NaHCO_3 and $\text{Na}_2\text{CO}_3 \cdot 3\text{NaHCO}_3$ can form at 70°C . This is because the enthalpy of reaction is so high (roughly -30.8 kcal/gmol CO_2 reacted) that the particle is quickly heated to a temperature above 73°C at which NaHCO_3 will not form. The temperature at the reacting front at the surface of the particle initially, and in the interior of the particle later in the experiment, will be approximately 82.2 to 84°C . If the TGA experiment at 70°C had been carried out for a larger period of time, it would have been interesting to see if, as the formation of $\text{Na}_2\text{CO}_3 \cdot 3\text{NaHCO}_3$ slowed to completion and the outer regions of the particle cooled to 73°C or less, the dimensionless weight would have approached 1.00 (indicating complete carbonization to NaHCO_3). The TGA experiment carried out at 60°C and summarized in Figure 13 hints that this would be the case. As described above, the initial carbonization rate for the 60°C case is consistent with the formation of $\text{Na}_2\text{CO}_3 \cdot 3\text{NaHCO}_3$. Again this is due to the highly exothermic nature of the carbonization reactions resulting in particle surface temperatures greater than 73°C , the temperature above which NaHCO_3 will not form. As the reaction front moves into the interior of the particle, the surface region begins to cool to 73°C at which point NaHCO_3 begins to form. It is clear that for an experiment carried out at 60°C gas temperature, the time at which the surface could reach 73°C would be significantly shorter than in the case of an experiment carried out at a gas temperature of 70°C (which is very close to the upper temperature limit of stability of NaHCO_3). As can be seen from Figure 13, the weight gain curve for the experiment carried out at 60°C gas temperature is extremely complex and should prove a challenge to explain. As mentioned above, the dimensionless weight gain curve for 70 and 80°C seem to follow carbonization kinetics that appear to be first order with respect to the amount of unreacted Na_2CO_3 remaining in the particle; however, there may be other explanations for the kinetic behavior that remain to be explored.

The above analyses of the carbonization rate in the TGA experiments serve to point out the need for accurate thermodynamic data for the Na_2CO_3 , NaHCO_3 , $\text{Na}_2\text{CO}_3 \cdot 3\text{NaHCO}_3$, CO_2 and steam system. Resolution of the thermodynamic data would allow better estimates of the rate of carbonization of Na_2CO_3 for a given bulk gas composition and may resolve questions concerning composition of the carbonization end product.

5.0 CONCLUSIONS AND FUTURE WORK

Thermogravimetric analyses of cyclic calcination/carbonation reactions with sodium bicarbonate as a sorbent precursor indicated that the severity of calcination has an effect on the subsequent carbonation activity. These effect is more pronounced at low extents of carbonation and also in the earlier cycles.

Fluidized bed testing using trona as a sorbent precursor indicated that it is less active than sodium bicarbonate. Second cycle carbonation activity appeared to decline more significantly than in previous tests using sodium bicarbonate as a sorbent precursor.

Thermodynamic analyses of previous data suggest that $\text{Na}_2\text{CO}_3 \cdot 3\text{NaHCO}_3$ may be the primary reaction product for carbonation reactions conducted above 73°C , and an important reaction product for lower temperature reactions.

In the next quarter LSU will continue electrobalance and fixed bed studies of carbonation reaction kinetics, including the effect of calcination conditions. RTI will conduct additional fluidized bed tests with additional water added near the top of the fluidized bed. Preliminary transport reactor operating parameters will be determined.

LSU will continue work to determine the reaction mechanisms of the carbonation reaction, using both the electrobalance and the fixed bed reactor system. RTI will conduct additional cyclic fluidized bed tests on sodium bicarbonate. RTI and C&D will begin work related to design of a transport reactor system for the carbonation phase of the cycle. Additional thermodynamic investigations of the potential for cyclic processes using phases intermediate between sodium carbonate and sodium bicarbonate will be conducted. A meeting is planned in January to review the project program.

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).

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., 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, July 2001(c).

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

Lewis, G. N. and Randall, M., Thermodynamics and the Free Energy of Chemical Substances, McGraw Hill, 1923.

Perry, J. H., et al., Chemical Engineers' Handbook, McGraw Hill, 1963.