CARBON DIOXIDE CAPTURE FROM FLUE GAS USING DRY REGENERABLE SORBENTS

QUARTERLY TECHNICAL PROGRESS REPORT

Reporting Period: January 1, 2004 to March 31, 2004

by
David A. Green
Brian S. Turk
Jeffrey W. Portzer
Raghubir P. Gupta
William J. McMichael
Thomas Nelson

Submitted by:

Research Triangle Institute
Post Office Box 12194
Research Triangle Park, NC 27709-2194

April 2004

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United State Government or any agency thereof. The views and opinions of authors expressed therein do not necessarily state or reflect those of the United States Government or any agency thereof.

ABSTRACT

This report describes research conducted between January 1, 2004 and March 31, 2004 on the use of dry regenerable sorbents for removal of carbon dioxide from flue gas. RTI has produced laboratory scale batches (approximately 300 grams) of supported sorbents (composed of 20 to 40% sodium carbonate) with high surface area and acceptable activity. Initial rates of weight gain of the supported sorbents when exposed to a simulated flue gas exceeded that of 100% calcined sodium bicarbonate. One of these sorbents was tested through six cycles of carbonation/calcination by thermogravimetric analysis and found to have consistent carbonation activity. Kinetic modeling of the regeneration cycle on the basis of diffusion resistance at the particle surface is impractical, because the evolving gases have an identical composition to those assumed for the bulk fluidization gas. A kinetic model of the reaction has been developed on the basis of bulk motion of water and carbon dioxide at the particle surface (as opposed to control by gas diffusion). The model will be used to define the operating conditions in future laboratory- and pilot-scale testing.

TABLE OF CONTENTS

Page

LIST OF FIGURES

LIST OF TABLES

Table   **Page**
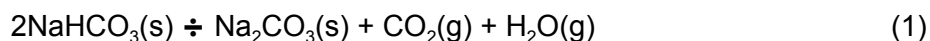
1.0 EXECUTIVE SUMMARY

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 alkali carbonates, and particularly sodium carbonate, which is converted to bicarbonate or an intermediate salt through reaction with carbon dioxide and water vapor. Bicarbonate is regenerated to carbonate when heated, producing a nearly pure CO_2 stream after condensation of water vapor.

This quarter, seventeen sorbents composed of 20 to 40% sodium carbonate on a support were prepared by spray drying. The supported sorbents had greater surface areas and activities than calcined grade 3 sodium bicarbonate (SBC#3). One sorbent was tested through six cycles by thermogravimetric analysis and found to maintain its carbonation activity. Mathematical modeling activities this quarter concluded that calcination in a 50/50 mixture of carbon dioxide and water vapor would take place at approximately 107°C (224°F) or higher.
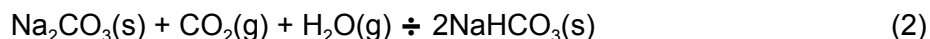
2.0 INTRODUCTION

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:

$$2NaHCO_3(s) \rightleftharpoons Na_2CO_3(s) + CO_2(g) + H_2O(g) \tag{1}$$

and

$$Na_2CO_3(s) + CO_2(g) + H_2O(g) \rightleftharpoons 2NaHCO_3(s) \tag{2}$$

Reaction (1) releases CO_2 and regenerates the sorbent, while Reaction (2) is used to capture CO_2. Other solid products, intermediate between sodium carbonate and sodium bicarbonate, may also be produced under the anticipated reaction conditions. An intermediate compound, $Na_2CO_3 \cdot 3NaHCO_3$, known as Wegscheider's salt, forms at the reaction conditions of interest.

The carbon dioxide capture reaction is exothermic and the sorbent regeneration reaction (calcination) is endothermic, and takes place at a slightly higher temperature. The sorbent can be recycled numerous times. Traces of SO_2 and HCl, which may be present in desulfurized flue gas from coal-fired power plants, will react irreversibly with the sorbent.

1

This report describes activities conducted between January 1, 2004 and March 31, 2004 by RTI and its subcontractor Church and Dwight (C&D). Activities conducted this quarter include development of improved spray dried supported sorbents and mathematical modeling of reaction kinetics.

3.0 EXPERIMENTAL

3.1 Sorbent Preparation

A total of 17 different sorbents were produced this quarter composed of sodium carbonate supported on a ceramic material. Small batches were made by co-precipitation, followed by pressure filtration. The materials were spray dried, and in most cases calcined at 450ΕC for two hours. Spray dryer parameters, including additive composition, nozzle size and nozzle projection were varied in an attempt to produce high surface area, high density (attrition resistant) particles. The BET surface areas and Davison attrition indexes of these sorbents were determined. The carbonation activities were evaluated by thermogravimetric analysis (TGA).

3.2 Thermogravimetric Testing of Supported Sorbents

The supported sorbents were screened by thermogravimetric analysis to determine their relative carbonation activity. These tests were conducted at 70ΕC in an atmosphere of 8.3% carbon dioxide and 6.5% water vapor. Weight gain over the initial 20 minute period of exposure to the carbonation gas was used to compare the different formulations.

4.0 RESULTS AND DISCUSSION

4.1 Properties of Supported Materials

Seventeen supported sodium carbonate sorbents were prepared this quarter. The compositions and selected properties of these materials are shown in Table 1. All of the supported sorbents produced this quarter had BET surface areas that were much greater than that of calcined SBC#3, however none of the materials produced had attrition resistance comparable to that of conventional fluidized bed catalytic cracking catalysts. Calcined SBC#3 has a BET surface area of 2.41 m^2/g, while the 20% sodium carbonate materials listed in Table 1 had BET surface areas ranging from 25 to 80 m^2/g, and the 40% supported sodium carbonate materials had BET surface areas of 13 to 15 m^2/g. Changes to spray dryer nozzle diameters and nozzle projections did not result in improvements to the surface areas of the supported catalysts.

Table 1. Properties of Supported Sodium Carbonate Sorbents

Sample #	Amount Na2CO3 added (%)	Spray Dry?	BET Surface Area (m^2/g)	Weight gain (%)	Attrition (DI)
010904-1	20	No	N/A	7.8	N/A
011304-1	20	No	N/A	8.2	N/A
021104-1a, -1b	20	Yes	25.2	23.4	N/A
022404-1	20	Yes	29.9	6.1	N/A
030204-1	20	Yes	66.21	4.6	47
030304-1	20	Yes	51.99	5.5	53.7
031004-1	20	Yes	49.36	6.6	74.7
031104-1	40	Yes	17.24	13.6	72.4
031204-1	20	Yes	79.82	5.6	68.5
032304-1	20	Yes	39.13	10.8	68.97
032304-4	40	Yes	13.86	13.9	N/A
032404-1	20	Yes	71.61	6.4	N/A
040204-1a	20	Yes	28.43	7	N/A
040504-1a	40	Yes	12.91	10	N/A
040804-1a	20	Yes	33.7	N/A	N/A
040904-1a	40	Yes	14.29	N/A	N/A
041204-1a	20	Yes	31.4	N/A	N/A
SBC 3	---	----	2.41	10.6	N/A
Typical FCC Catalyst	---	----	----	----	23.37

N/A = not available

4.2 TGA Testing of Supported Sorbents

The supported sorbents produced this quarter were screened for activity by TGA at 70EC in an atmosphere of 8.3% carbon dioxide and 6.5% water vapor. Prior to carbonation, the samples were heated to 150EC in helium to eliminate the effects of moisture gain and adsorption of atmospheric gases (including carbon dioxide). Weight gains resulting from conversion of sodium carbonate in the sorbent to Wegscheider's salt over an arbitrary 20 minute calcination time were used to compare sorbent activity. Weight gains for the 20% sodium carbonate sorbents ranged between 8% and 23%. The 40% sodium carbonate sorbents gained between 10 and 14% in weight over 20 minutes. This contrasts with unsupported sodium carbonate produced by calcining SBC#3 which gained 10.6% in weight over the same 20 minute period. The fact that the supported sorbents are as active as the 100% sodium carbonate (and in many

cases more active) even though they contain only 20 to 40% as much reactant is consistent with the increased surface area. Weight gains are listed in Table 1.

The supported sorbents exhibited a rapid initial weight gain upon exposure to the carbonation gas mixture. Figure 1 contrasts the initial carbonation weight gain of sample 021104-1a with calcined SBC#3. The SBC#3 shows a greater long term weight gain, however the supported sorbents offer a faster initial rate which is more important for short residence time fast-fluidized bed type contacting equipment.
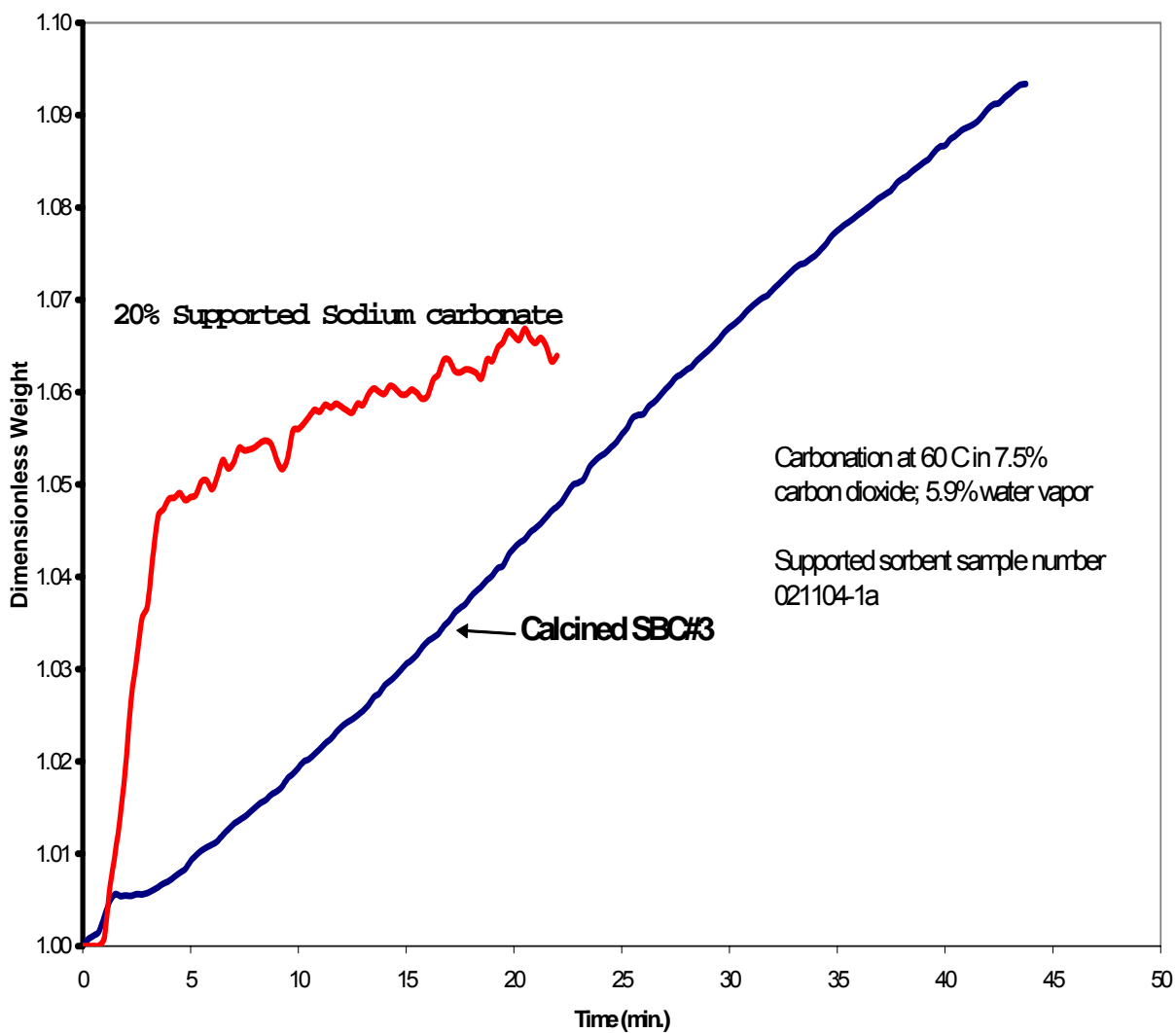

Figure 1. Carbonation of calcined SBC#3 and 20% supported sodium carbonate

A sample of a different supported sorbent was subjected to six cycles of calcination/ carbonation in the TGA. This material, was composed of 20% sodium carbonate/ 80% support. The sample was precalcined in helium at 150 EC to remove residual moisture and other

adsorbed gases. Data are shown in Figure 2. Carbonation was conducted at 70℃ in an atmosphere of 8.3% carbon dioxide/6.5% water vapor. In the first carbonation cycle, the sorbent rapidly gained about 6% in weight. Subsequent calcination (at 150℃ in helium) was not sufficient to completely reverse this weight gain. Over six cycles, the sorbent gradually lost sorption capacity (as seen by the increasing weights after calcination. The sixth carbonation cycle included a rapid weight gain of about 3%. The rates of carbonation during the rapid weight gain phase of the carbonation cycle, indicated by pairs of horizontal marks in Figure 2, are shown in Figure 3. These rates (as indicated by the slope of the weight gain curve between the markings in Figure 2) are stable, even though the capacity of the sorbent appears to decrease with subsequent cycles.
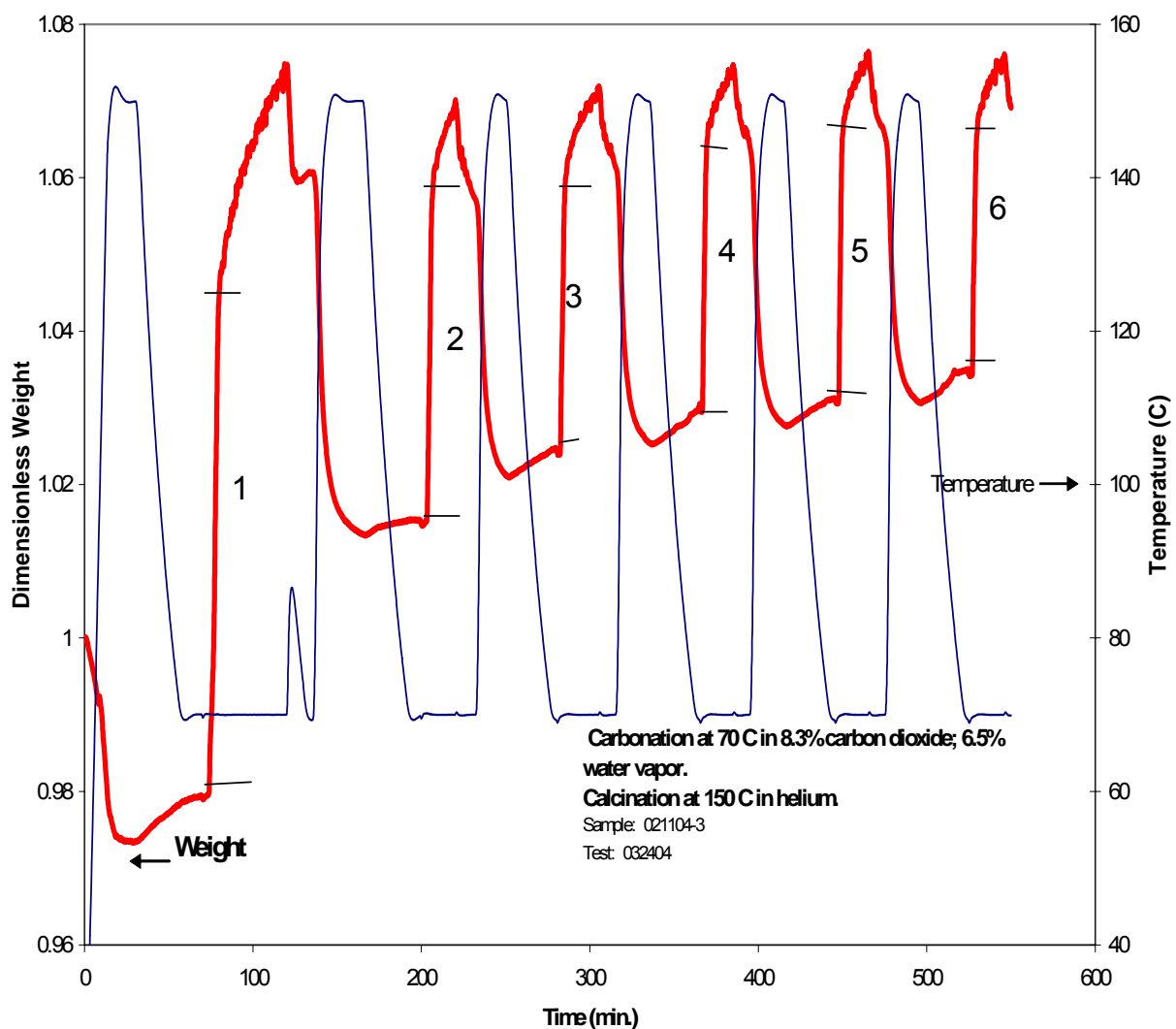

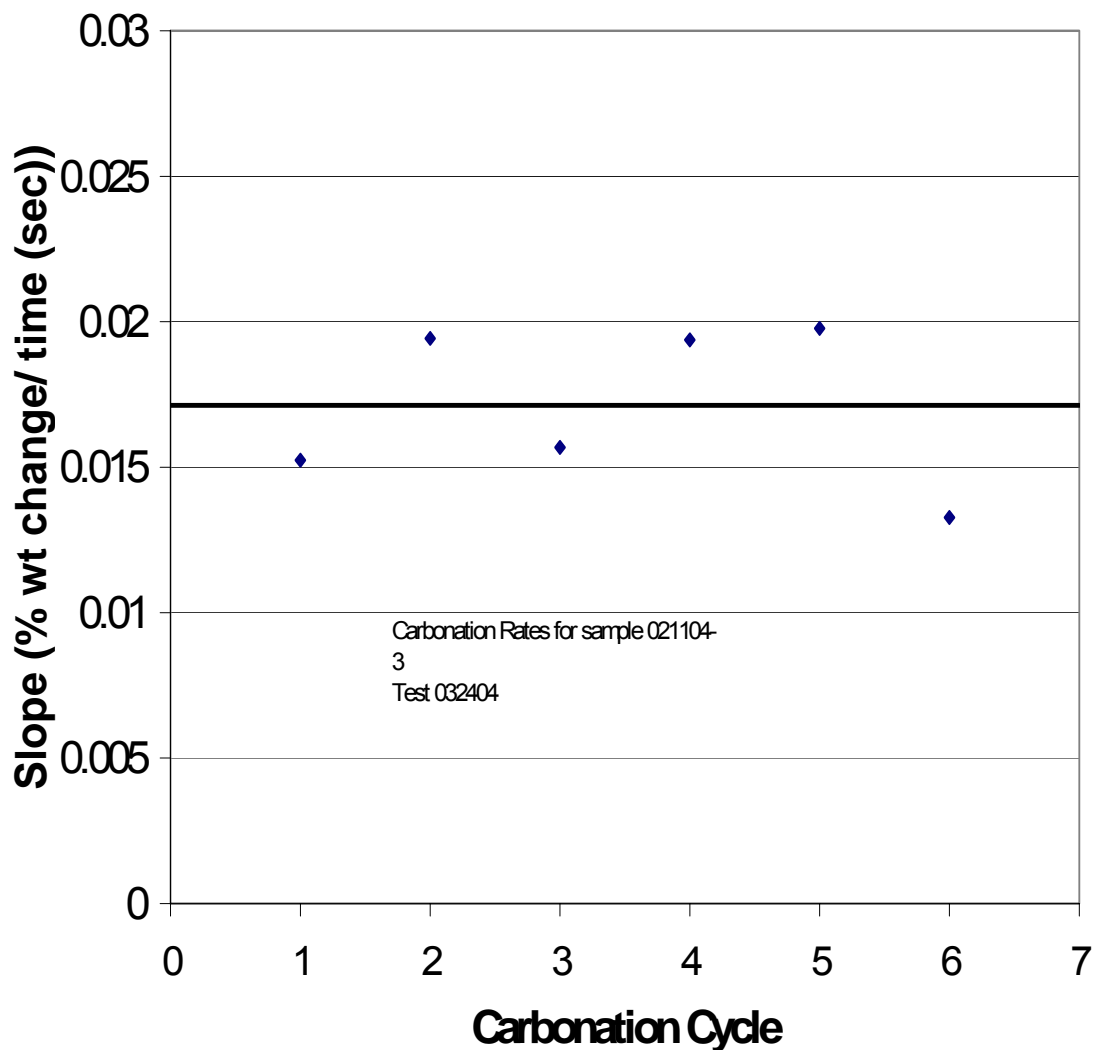**Figure 2. Multicycle carbonation of 20% supported sodium carbonate**

Figure 3. Rate of rapid carbonation phase over six cycles

4.3 Process Modeling: Regeneration of Na$_2$CO$_3$ Based Sorbents

A simplified flow sheet of the RTI dry sorbent CO$_2$ removal process is shown in Figure 4. The flow sheet shown in Figure 4 is one of the possible flow configurations. As shown in the figure, absorption of CO$_2$ from flue gas is carried out in the fast fluidized bed carbonizer where CO$_2$ and water vapor react with regenerated sorbent, containing mostly Na$_2$CO$_3$ as the sodium specie, to form Wegscheider's salt by the following reaction:
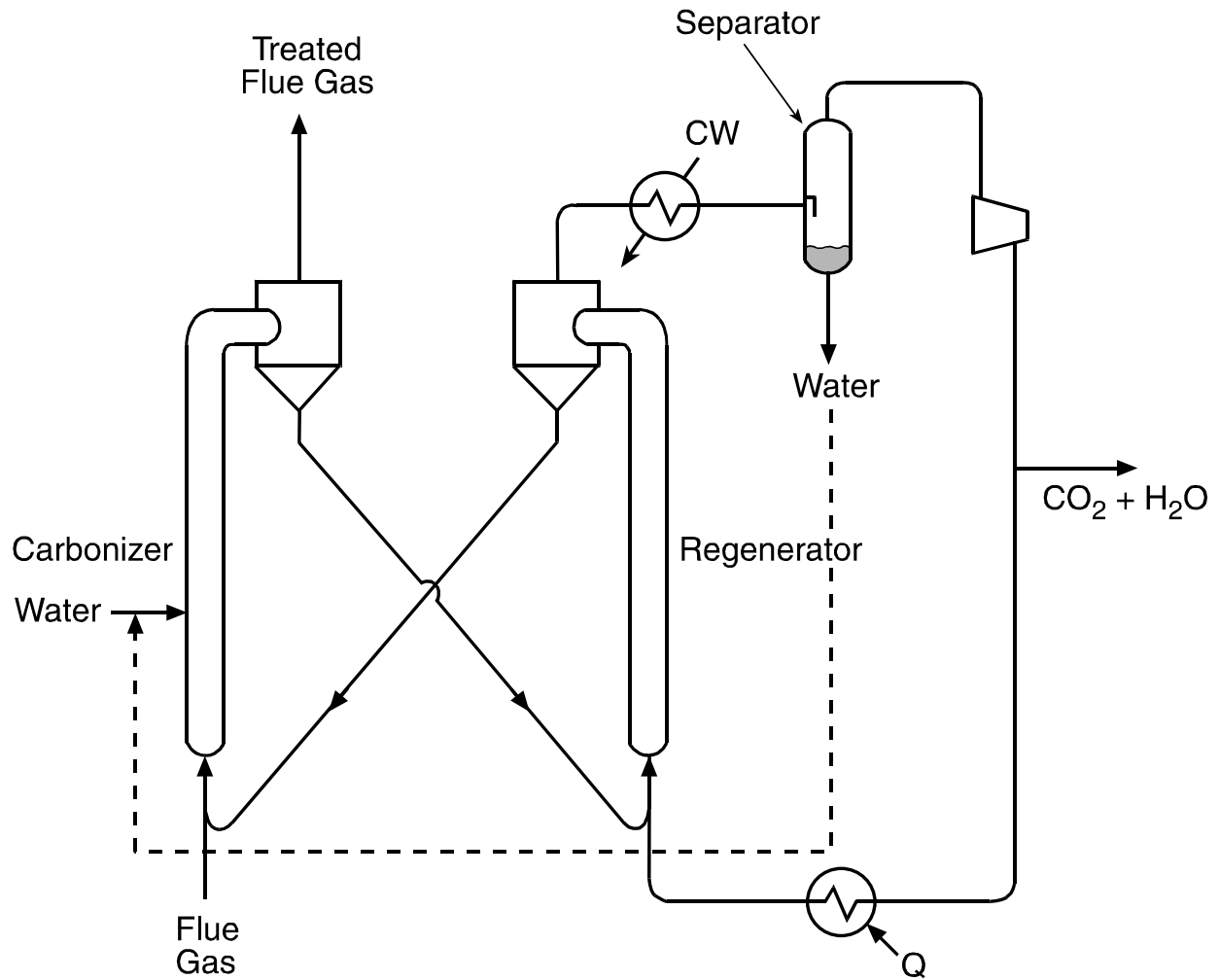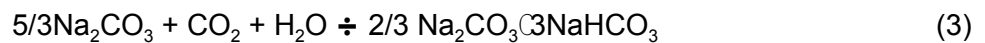
6

Figure 4. Simplified process flow diagram

$$5/3 Na_2CO_3 + CO_2 + H_2O \rightleftharpoons 2/3\ Na_2CO_3 \cdot 3NaHCO_3 \tag{3}$$

The reaction is highly exothermic; and therefore, the favorability of the reaction decreases with an increase in reaction temperature. The equilibrium constant for Reaction 3 is given by

$$K = \frac{1}{P_{CO_2} P_{H_2O}} \tag{4}$$

where K is the equilibrium constant and P_{CO2},
and P_{H2O} are the partial pressures of CO_2 and water vapor, respectively, atm.

Based on thermodynamics, the equilibrium constant, K, is roughly a function of temperature only (at low pressure). Given the partial pressure of CO_2 and water vapor at the surface of a

7

Na_2CO_3/Wegscheider's salt mixture, the equilibrium constant can be calculated by Equation 4 and from that, an equilibrium temperature, T_{eq}, found that satisfies Equation 4.

If the temperature of the solid Na_2CO_3/Wegscheider's salt mixture, T_o , is less than T_{eq}

$$T_o < T_{eq} \tag{5}$$

then carbonization will take place. On the other hand, for

$$T_o > T_{eq} \tag{6}$$

then regeneration, or the reverse of Reaction 3 will take place.

In the carbonizer, for initial flue gas compositions and temperatures that might be encountered in practice, and because of the highly exothermic nature of the carbonization reaction, only low CO_2 removal efficiencies are achievable without a high degree of heat removal or heat absorption from the carbonizer. In order to moderate the temperatures in the carbonizer and to keep the carbonization reaction favorable, liquid water is injected into the carbonizer. Evaporation of this water absorbs the exothermic heat of the carbonization reaction and also adds valuable reactant, water vapor, to the carbonizer which helps force the absorption of CO_2 from the flue gas.

Based on preliminary heat and material balances associated with the flow sheet shown in Figure 4, it is estimated that the loaded sorbent leaving the carbonizer will have a temperature of roughly 185°F. This loaded sorbent is sent to the regenerator where the Wegscheider's salt produced in the carbonizer is converted back to Na_2CO_3. The temperature to which the loaded sorbent must be heated to initiate regeneration is highly dependent on the composition of the recycled regenerator gas. This gas will be a mixture of CO_2 and water vapor with CO_2 being 50% or greater depending on how much effort is expended to cool the recycle gas and condense out water as shown in Figure 4. The concentration of CO_2 at which the regeneration gas cooler and condensate trap can be eliminated is 50%. Thus, operating the regenerator with a 50/50 mixture of CO_2 and water vapor would eliminate an expensive heat exchanger and eliminate considerable recycle gas reheat energy.

Assuming that the regenerator operates at a total pressure of roughly 1 atm with a recycle gas containing a 50/50 mixture of CO_2 and water vapor, Equation 4 can be used to find that the equilibrium temperature, T_{eq}, at such conditions would be 224°F. Thus, as discussed above, the sorbent temperature must be raised to at least 224°F for regeneration to take place. Since, the loaded sorbent enters the Regenerator at roughly 185°F, some carbonization will take place in the regenerator until the sorbent temperature reaches or exceeds 224°F at which point regeneration will take place.

For the CO_2 removal configuration shown in Figure 4, with the recycle gas entering the bottom of the regenerator at about 600°F and the loaded sorbent entering at 185°F, it is anticipated that the temperature profiles in the fast fluidized regenerator will resemble those shown in Figure 5. The exact nature of these profiles depends on rate of the carbonization reaction and heat and mass transfer considerations.
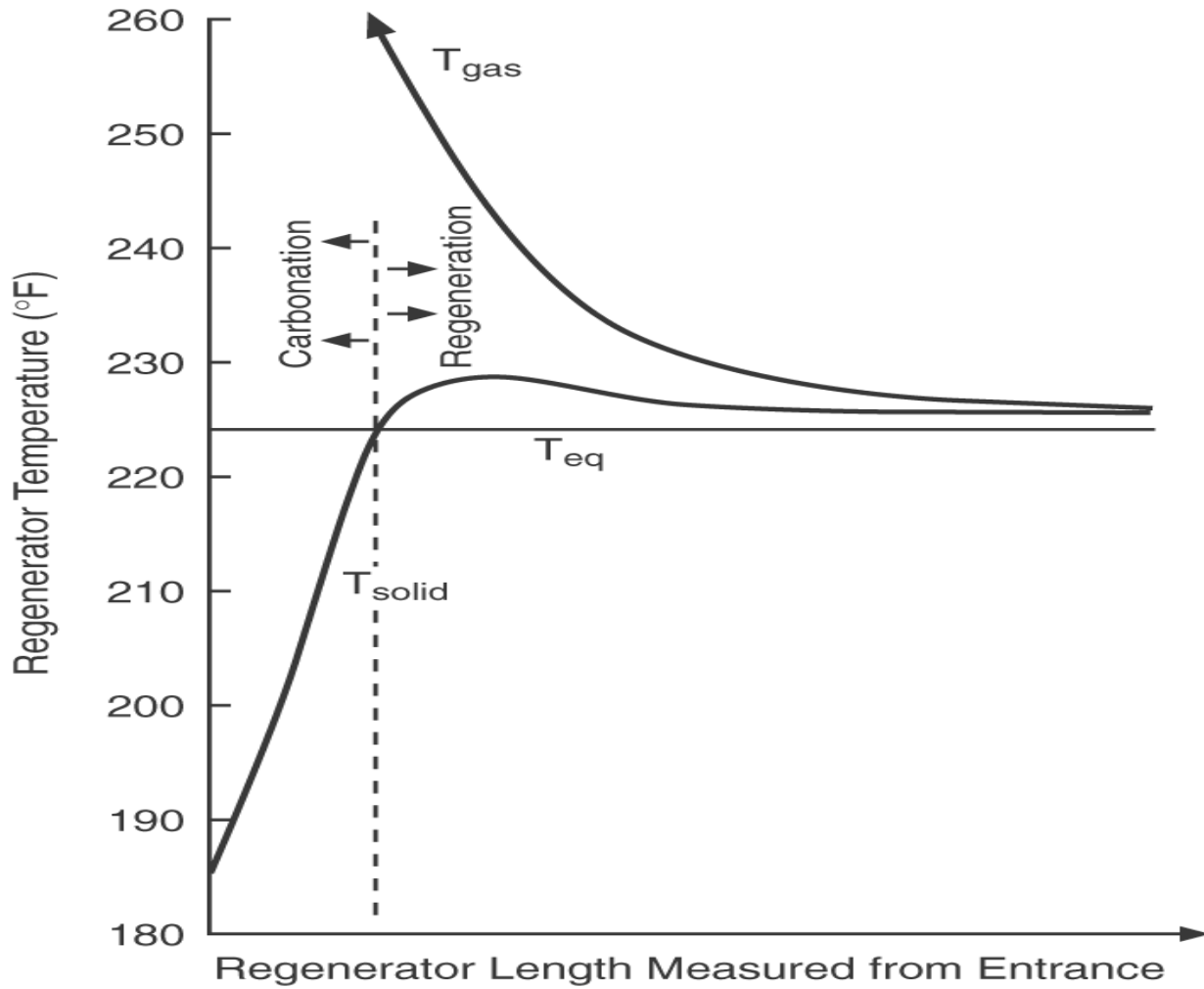
Figure 5. Anticipated temperature profiles in the regenerator

In the treatment of the regenerator given below, it is assumed that the rate of carbonization or regeneration is fast enough that equilibrium of Reaction 3 is established at the solid surface. This assumption was found to be valid in RTI's TGA experiments: however, at present, kinetic data for small sorbent particles in the fast fluidized bed environment are lacking. Assuming equilibrium of Reaction 3 in the solid makes the calculation of the rate of regeneration (or carbonization) a balance between heat and mass transfer effects.

Estimates of possible mass transfer rates can be obtained using particle/gas mass transfer coefficients:

$$N_{CO_2} = k_x (X^{\circ}{}_{CO_2} - X^{\infty}{}_{CO_2}) + X^{\circ}{}_{CO_2} (N_{CO_2} + N_{H_2O}) \tag{7}$$

where N_{CO2}, N_{H2O} are the fluxes of CO_2 and water vapor, respectively, lbmol/(ft^2 hr),

XE_{CO2} and X^4_{CO2} are the mole fractions of CO_2 in the gas at the particle surface and in bulk gas phase, respectively, and k_x is the mass transfer coefficient, lbmol/(ft^2 hr).

The mass fluxes, N_{CO2} and N_{H2O}, are positive for the movement of CO_2 and H_2O away from surface into the bulk fluid.

The mass transfer coefficient defined by Equation 7 is such that first term on the right hand side of Equation 7 represents the diffusional flux of CO_2 relative to the bulk motion of the gases. Defined in this way, the mass transfer coefficient, can be calculated by analogy from correlations for heat transfer coefficients.

For the case of regeneration (or carbonization) of the Na_2CO_3 based sorbent by Reaction 3, the fluxes of CO_2 and water vapor will be equal:

$$N_{H_2O} = N_{CO_2} \qquad (8)$$

Under this condition Equation 9 can be rewritten as :

$$N_{CO_2} = K_x \frac{(X^{\circ}_{CO_2} - X^{\infty}_{CO_2})}{(1 - 2X^{\circ}_{CO_2})} \qquad (9)$$

Here it can be seen that as the mole fraction of CO_2 at the surface of the particle approaches 50%, the CO_2 flux may become quite large. Bird et al. (1960) using film theory, show that mass transfer away from the surface into bulk gas decreases mass and heat transfer coefficients, and mass transfer toward the surface increases transfer coefficients. Their results can be summarized as follows.

$$\frac{k_x^{\bullet}}{k_x} = \frac{\ell n(R+1)}{R} \qquad (10)$$

where k_x^C is the mass transfer coefficient at high mass flux, lbmol/ft^2 hr)

and the term, R, is defined as

$$R = \frac{X^{\circ}_{CO_2} - X^{\infty}_{CO_2}}{\dfrac{N_{CO_2}}{N_{CO_2} + N_{H_2O}} - X^{\infty}_{CO_2}} \qquad (11)$$

For situations of high mas fluxes, the mass transfer coefficient, k_x, in Equations 7 and 9, should be replaced by the high flux mass transfer coefficient, k_x^C

Again, noting that the fluxes of CO_2 and water vapor are equal, and adjusting the mass transfer equation, Equation 9, for high mass fluxes gives

$$N_{CO_2} = \tfrac{1}{2} \, k_x \, \ell n \, (R + 1) \qquad (12)$$

Thus the fluxes of CO_2 and water vapor can be calculated if the mole fractions of CO_2 in the bulk gas, X^4_{CO2}, and at the surface, X^E_{CO2}, are known.

Based on the previous assumption of equilibrium of Reaction 3, the conversion of Na_2CO_3 to Wegscheider's salt, and vice versa, the mole fraction of CO_2 at the surface can be calculated if the temperature and total pressure at the surface can be determined. Assumption of equilibrium of Reaction 3 at the particle surface implies:

$$(P_o X^\circ_{CO_2}) \; (P_o X^\circ_{H_2O}) = \frac{1}{K} \qquad (13)$$

where P_o is the total pressure at the surface.

Replacing X^E_{H2O} by

$$(X^\circ_{H_2O}) = (1 - X^\circ_{CO_2}) \qquad (14)$$

in Equation 13 and solving for X^E_{CO2} gives

$$X^\circ_{CO_2} = \frac{1 \pm \sqrt{1 - 4 / (P_o{}^2 K)}}{2} \qquad (15)$$

So, as long as $P_o{}^2 K > 4$, the mole fraction of CO_2 will be real and one root given by Equation (15) will be greater then 50% and the other less than 50%. Since it has been argued above that the regenerator recycle gas will contain 50% or greater mole fraction of CO_2, the most useful root given by Equation (15) is the one with the positive square root. Thus, between the extremes of the mole fraction CO_2 at the surface and in the bulk gas phase, the mole fraction will not approach 50% which, mathematically, would yield indeterminant mass fluxes in the film surrounding the particle.

Assuming that the total pressure, P_o, at the surface is roughly 1 atm, the mole fraction of CO_2, X^E_{CO2}, has been calculated as a function of sorbent temperature. These results are shown in Figure 6.
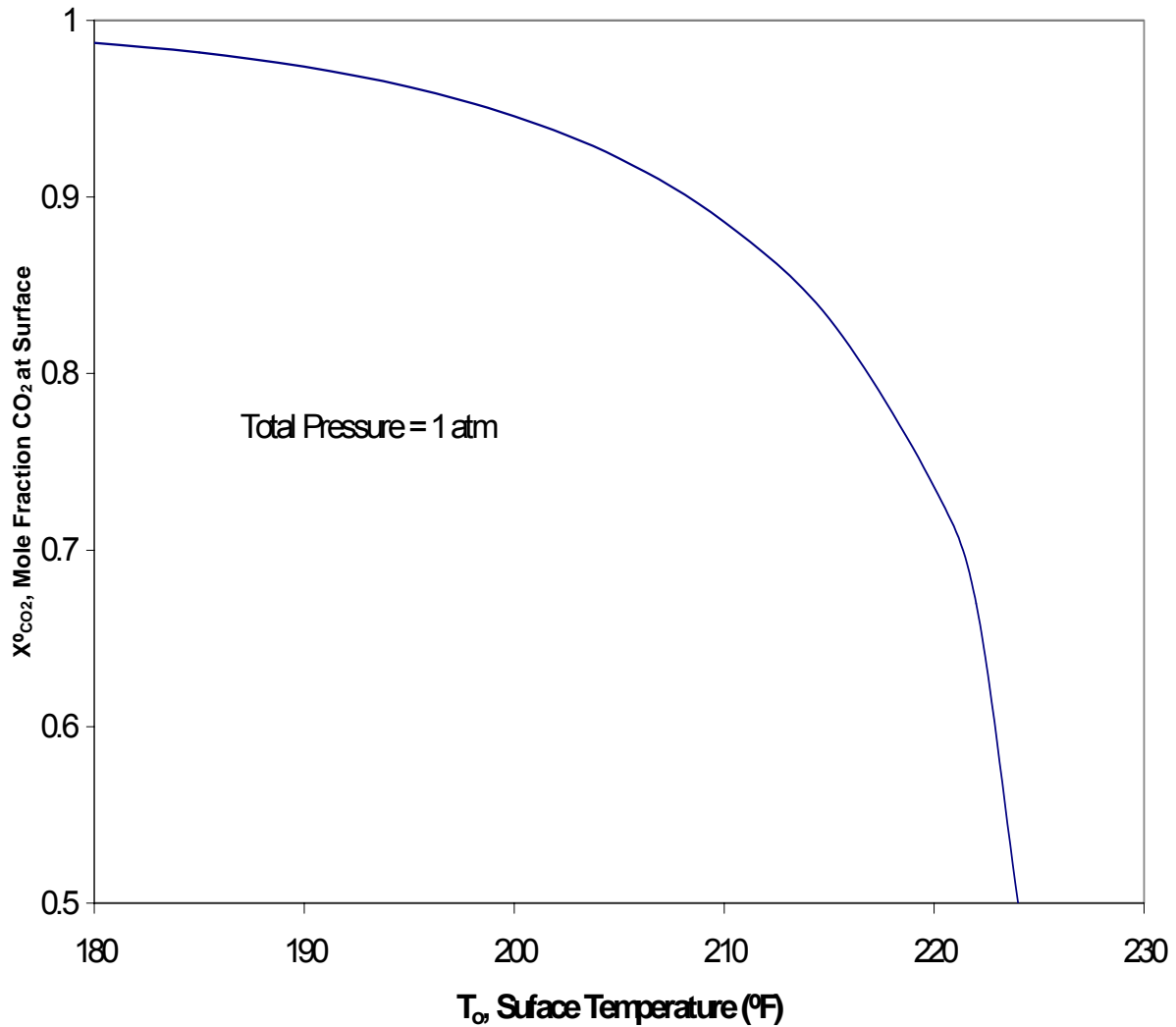
1

0.9

0.8

0.7

0.6

0.5

180   190   200   210   220   230

$X^o_{CO_2}$, Mole Fraction CO_2 at Surface

T_o, Suface Temperature (°F)

Total Pressure = 1 atm

Figure 6.   Dependence of mole fraction CO_2 on surface temperature at equilibrium of Reaction 1, the conversion of Na_2O_3 to Wegscheider's Salt

Using the results demonstrated in Figure 6, and using Equations 11 and 12 and given the bulk gas mole fraction of CO_2, $X^4_{CO_2}$, the mass flux of N_{CO2} can be calculated. Since the mole fraction of CO_2 entering with the recycle can be arbitrarily set (with some difficulty, as described above) the flux of CO_2 in an element of the regeneration reactor depends not only on the prescribed entering CO_2 concentration, but also on operating conditions and parameters. However, if the inlet concentration of CO_2 in the recycle gas is 50 mole percent, then it can be seen from Equation 11 that

$$R = \frac{X^{\circ}_{CO_2} - X^{\infty}_{CO_2}}{\frac{1}{2} - X^{\circ}_{CO_2}} = -1 \tag{16}$$

Regardless of the concentration of CO_2 at the sorbent/gas interface, $X^E_{CO_2}$, the mass flux of CO_2 by Equation 10 is -4. Thus, as the hot regenerator recycle gas at 50 mole percent CO_2 mixes at the entrance of the regenerator with loaded sorbent at 185°F, standard diffusion theory would predict infinite fluxes of CO_2 and water vapor from the bulk gas to the sorbent. This infinite flux of CO_2 and water vapor would be also accompanied by infinite heat release at the sorbent which would quickly raise the temperature of the sorbent above 224°F (for 1 atm total pressure at the surface of the sorbent). At this point the flux of CO_2 and water vapor should reverse and regeneration will take place.

The fact that conventional diffusion theory predicts infinite fluxes for the important case of X^4_{CO2} = 0.5 perhaps indicates that diffusional theory is no longer valid under this condition (although in its development as described by Bird et al. (1960), no such restriction on bulk gas concentration is implied). The fact that the computed fluxes are infinite might indicate that the transfer of CO_2 and water vapor is accomplished by bulk motion of gaseous components rather than by diffusional processes when the bulk gas concentration of CO_2 is equal to 50 mole percent (or closely approaches this limit).

Bulk gas motion about a sorbent particle can be envisioned as being driven by the pressure difference between the particle and the bulk gas. Under this condition, and assuming that an average gas viscosity can represent the variable viscosity in the gas film, the equation of motion for the gas moving in the radial direction about a spherical sorbent particle is given by

$$\rho u \frac{du}{dr} = -g_c \frac{dp}{dr} + \mu \left[\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{du}{2r} \right) - \frac{2n}{r^2} \right] \tag{17}$$

where ρ is the fluid density, lb/ft^3
         u is the radial velocity ft/sec
         p is the fluid pressure, lb/f/ft^2
         μ is the average fluid viscosity, lb/(ft sec)
         g_c is conversion factor 32.2 lb ft/sec^2 lb$_f$, and
         r is distance measured from the center of the sorbent particle, ft

The continuity equation for the system under consideration is given by

$$\frac{d}{dr}(\rho r^2 u) = 0 \tag{18}$$

This equation implies that

$$\rho r^2 u = C_1 \tag{19}$$

where C_1, is a constant

13

Assuming further that the fluid density, ρ, in the film surrounding the particle can be replaced by an average density and substituting Equation 19 into Equation 17 yields

$$\rho u \frac{\partial u}{\partial r} = -g_c \frac{\partial p}{\partial r} \tag{20}$$

Integrating both sides Equation 20 from the surface of the sorbent particle, r=R$_\rho$, to r=4 and assuming

$$u \to o \ as \ r \to \infty \tag{21}$$

gives

$$P_2 \, u_o^2 = g_c(P_o - P_\infty) \tag{22}$$

where u_o is the radial velocity at the surface of the spherical sorbent particle, ft/sec, and p_o, p_4 are the total pressures at the surface of the sorbent particle and the bulk gas, respectively, lb_f / ft^2

The flux of CO_2 can then be calculated from Equation 22 as follows

$$N_{CO_2} = \rho u_o = \sqrt{2g_c(P_o - P_\infty)\rho} \tag{23}$$

As long as $P_o > P_4$, the calculation of the CO_2 flux by Equation 23 appears to be straightforward, however if $P_o < P_4$ it would appear that the flux would be imaginary and would not have physical significance. In the absence of a mathematical explanation, the following is proposed for the case where $P_o < P_4$

$$N_{CO_2} = -\sqrt{2g_c(P_\infty - P_o)\rho} \tag{24}$$

Equation 24 does not satisfy the equation of motion, Equation 20.

For a regenerator recycle gas containing 50 mole percent CO_2, it has been argued above that the motion of CO_2 and water vapor to or from the particle is a result of bulk motion. Under this condition, it is anticipated that at the surface of the particle, CO_2 would be 50 mole percent. Under the conditions of equilibrium of the Na_2CO_3/Wegscheider's salt reaction, the equilibrium condition, Equation 4, becomes

$$P_o(0.50) P_o(0.50) = \frac{1}{K} \tag{25}$$

Thus,

$$P_o = 2\sqrt{1/K} \qquad (26)$$

It is interesting to note that the specification of the surface pressure, P_o given by Equation 24 yields a real root for surface mole fraction of CO_2, X^E_{CO2}, from Equation 15, with that mole fraction being 0.50 regardless of surface temperature, T_o. Using Equations 23 or 24 and 26, the flux of CO_2 to or from the surface can be computed as a function of the surface temperature, T_o, and bulk gas pressure, P_4. As reported previously (Green, et al., 2002) the equilibrium constant, K, is given roughly by

$$K = 4.090 \times 10^{-19} \exp\{29110/T\} \qquad (27)$$

where T is the reaction temperature, $°R$

To estimate the magnitude of the fluxes calculated by Equation 23, 25, and 27 an example follows. Assume that the recycled regenerator gas is a 50/50 mixture of CO_2 and water vapor, that at some point of interest in the regenerator the bulk gas pressure, P_4, is 1 atm and that the sorbent particle temperature, T_o, is 224°F. Under these conditions the CO_2 flux at the sorbent particle would be calculated through the use of Equations 23, 26, and 27 to be zero. However, if all the conditions described in the above example are held the same except that the particle temperature, T_o, is increased to 225°F the CO_2 flux would be + 1008 lbmolCO_2/(ft^{2}hr), an extremely large flux. At this regeneration rate, the amount of heat required to maintain a particle temperature of 225°F would be:

$$1008 \frac{lbmol\ CO_2}{ft^2\ hr} \times \frac{59420\ Btu}{lbmol\ CO_2} = 5.990 \times 10^7 \frac{Btu}{ft^2\ hr} \qquad (28)$$

In the regenerator, this heat would need to supplied by heat transfer from the gas phase. For 100F diameter sorbent in the fast fluidized environment the gas/solid heat transfer coefficient, h, is estimated to be 4.0 Btu/(ft^2 hr °F). Thus, to balance the heat requirement, the temperature difference between the sorbent and bulk gas would need to be

$$\Delta T = \frac{5.990 \times 10^7\ Btu/(ft^2 hr)}{4.0\ Btu/(ft^2 hr° F)} = 1.5 \times 10^{7\ \circ} F \qquad (29)$$

This is clearly impossible. For the example described above, the balance point between absorption of heat by regeneration and supply of heat by transfer from the gas phase would be somewhere between 1) 225°F; where the rate of heat absorption is astronomical and the temperature difference between the gas and solid would need to be 1.5×10^7°F, or 2) 224°F where nothing happens. Actually the operating point of the regeneration would be very close to 224°F. As a generalization of the above example it appears that regeneration rate would be

$$N_{CO_2} = \frac{h(T_\infty - T_{eq})}{\Delta H_{CO_2}} \qquad (30)$$

15

where T_{eq} is the equilibrium temperature, TЕF, satisfying

$$K(T_{eq}) = 4 / P_{\infty}^2 \qquad (31)$$

and ΔH_{CO2} is the enthalpy of regeneration, Btu/lb mol CO_2. Equation 31 has been derived for a regenerator recycle gas that is a 50/50 mixture of CO_2 and water vapor; however, it is likely to hold for a wide range of CO_2/water vapor recycle gas mixtures.

The results given by Equation 30 and 31 are consistent with the rate expressions derived to explain RTI's TGA results. In the coming quarter these expressions will be applied to simulating the regeneration. Such an approach could greatly simplify the calculation of regeneration rates and avoid undefined or infinite fluxes that arise in applying conventional mass diffusion theory.

4.4 Other Project Activities

Because of difficulties in locating a suitable facility for transport reactor testing, plans for construction of a skid mounted reactor system for connection to the Modular Carbon Capture Facility located at NETL in Pittsburgh are presently being developed.

5.0 CONCLUSIONS

Supported sorbents containing 20% sodium carbonate can be produced by spray drying which have surface areas 10 to 30 times greater than calcined SBC#3. The materials produced to date have less attrition resistance than conventional fluidized catalytic cracking catalysts which have a similar ceramic structure.

Supported sorbents containing 20 to 40% sodium carbonate have greater reactivity than calcined SBC#3, as indicated by TGA testing. The increase in reactivity has been demonstrated over the initial 20 minutes of the reaction. More significantly, reactivity of the supported sorbents is much greater in the first minute of exposure to simulated flue gas than the reactivity of calcined SBC#3. This is of great importance because the anticipated contacting schemes are likely to involve short residence time fast-fluidized bed reactor systems.

In multicycle TGA testing of one supported sorbent, a gradual decrease in capacity was observed over six calcination/carbonation cycles. The rate of initial weight gain did not exhibit a corresponding decrease.

Mathematical modeling of the regeneration of a sodium carbonate sorbent in a 50/50 mixture of carbon dioxide and water vapor indicates that the reactor temperature should be approximately 224ЕF.

6.0 FUTURE WORK

Dr. Gupta will make a presentation at the Global Climate and Energy Project Workshop on Carbon Capture and Sequestration at Stanford University in April, 2004

A poster presentation will be prepared for exhibit at the Third Annual Conference on Carbon Sequestration in Alexandria, Virginia in May, 2004.

A short fluidized bed reactor with an expansion section at the top will be designed for laboratory operation to determine the effect of extended operation on sorbent utilization and carbon dioxide removal efficiency.

Preliminary design calculations for construction of a module for use at the NETL modular carbon capture facility will be started.

7.0 REFERENCES

Bird, R. B., Stewart, W. E., and Lightfoot, E. N. Transport Phenomena. New York. 1960.

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