

CARBON DIOXIDE CAPTURE FROM FLUE GAS USING DRY REGENERABLE SORBENTS

TOPICAL REPORT

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ABSTRACT

Laboratory studies were conducted to investigate dry, regenerable, alkali carbonate-based sorbents for the capture of CO₂ from power plant flue gas. Electrobalance, fixed-bed and fluid-bed reactors were used to examine both the CO₂ capture and sorbent regeneration phases of the process. Sodium carbonate-based sorbents (calcined sodium bicarbonate and calcined trona) were the primary focus of the testing. Supported sodium carbonate and potassium carbonate sorbents were also tested.

Sodium carbonate reacts with CO₂ and water vapor contained in flue gas at temperatures between 60 and 80°C to form sodium bicarbonate, or an intermediate salt (Wegscheider's salt). Thermal regeneration of this sorbent produces an off-gas containing equal molar quantities of CO₂ and H₂O. The low temperature range in which the carbonation reaction takes place is suited to treatment of coal-derived flue gases following wet flue gas desulfurization processes, but limits the concentration of water vapor which is an essential reactant in the carbonation reaction. Sorbent regeneration in an atmosphere of CO₂ and water vapor can be carried out at a temperature of 160°C or higher. Pure CO₂ suitable for use or sequestration is available after condensation of the H₂O. Flue gas contaminants such as SO₂ react irreversibly with the sorbent so that upstream desulfurization will be required when sulfur-containing fossil fuels are used.

Approximately 90% CO₂ capture from a simulated flue gas was achieved during the early stages of fixed-bed reactor tests using a nominal carbonation temperature of 60°C. Effectively complete sorbent carbonation is possible when the fixed-bed test is carried out to completion. No decrease in sorbent activity was noted in a 15-cycle test using the above carbonation conditions coupled with regeneration in pure CO₂ at 160°C.

Fluidized-bed reactor tests of up to five cycles were conducted. Carbonation of sodium carbonate in these tests is initially very rapid and high degrees of removal are possible. The exothermic nature of the carbonation reaction resulted in a rise in bed temperature and subsequent decline in removal rate. Good temperature control, possibly through addition of supplemental water and evaporative cooling, appears to be the key to getting consistent carbon dioxide removal in a full-scale reactor system.

The tendency of the alkali carbonate sorbents to cake on contact with liquid water complicates laboratory investigations as well as the design of larger scale systems. Also their low attrition resistance appears unsuitable for their use in dilute-phase transport reactor systems. Sodium

and potassium carbonate have been incorporated in ceramic supports to obtain greater surface area and attrition resistance, using a laboratory spray dryer. The caking tendency is reduced and attrition resistance increased by supporting the sorbent. Supported sorbents with loading of up to 40 wt% sodium and potassium carbonate have been prepared and tested. These materials may improve the feasibility of large-scale CO₂ capture systems based on short residence time dilute-phase transport reactor systems.

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LIST OF ACRONYMS AND ABBREVIATIONS

AR	Attrition Ration
BET	Brunauer-Emmett-Teller
FID	flame ionization detector
HPLC	high-pressure liquid chromatography
LSU	Louisiana State University
MFC	mass flow controllers
SBC	sodium bicarbonate
TCD	thermal conductivity detector
PTFE	polytetrafluoroethane
PC	personal computer
ppm	parts per million
sccm	standard cubic centimeters per minute

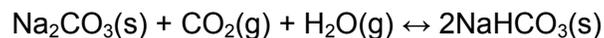
EXECUTIVE SUMMARY

This report contains information relating to research on the capture of CO₂ from flue gas using dry, regenerable, alkali carbonate-based sorbents. The research was sponsored by the U.S. Department of Energy, National Energy Technology Laboratory. RTI International¹ (RTI) was the prime contractor and Louisiana State University (LSU) served as subcontractor. Church and Dwight, Inc. was the industrial partner for the project.

Combustion of fossil fuels since the beginning of the industrial revolution is believed to be a major cause of the increased concentration of CO₂ in the atmosphere. It is becoming clear that improved energy efficiency and substitution of low-carbon fuels, while important, will not be sufficient to limit the growth of atmospheric CO₂ concentrations. New technologies for the capture and sequestration of CO₂ are needed.

The only currently available process for the capture of CO₂ from flue gas streams is based on amine scrubbing, a costly and energy-intensive process. The regenerable sorbent-based process being developed in this project provides an alternate to amine scrubbing. This process is applicable to the capture of CO₂ from existing fossil fuel-fired power plants and is potentially applicable to CO₂ capture from all stationary fossil fuel combustion sources.

The important reactions involved in the capture of CO₂ using sodium carbonate (Na₂CO₃) sorbents result in the reversible formation of sodium bicarbonate (NaHCO₃) and Wegscheider's salt (Na₂CO₃•3NaHCO₃):



and



Both forward reactions are exothermic. CO₂ capture is accomplished by the forward reactions while equal molar quantities of CO₂ and H₂O are produced by the reverse, or sorbent regeneration, reactions. Condensation of H₂O from the regeneration product gas results in a pure CO₂ product suitable for use or sequestration.

Laboratory studies of the CO₂ capture and regeneration reactions have been conducted in an electrobalance (thermogravimetric analyzer) and in bench-scale fixed-bed and fluidized-bed

¹ RTI International is a trade name of Research Triangle Institute.

reactor systems. Physical properties of sorbents including several grades of calcined sodium bicarbonate (SBC), calcined trona, and potassium carbonate have been determined.

Multicycle tests have been conducted to provide preliminary information on sorbent durability. The carbonation reaction was studied in the electrobalance between 60°C and 80°C using, in most cases, a feed gas containing 8% CO₂ and 16% H₂O, with the balance made up of an inert gas (either He or N₂). These CO₂ and H₂O contents simulate the flue gas formed from the complete combustion of CH₄ using 10% excess air. Calcination was studied between 120°C and 200°C in an atmosphere ranging from 0% CO₂ (100% inert) to 100% CO₂. Low-temperature calcination in an inert atmosphere, while not commercially feasible, was chosen to minimize the severity of the sorbent exposure during the calcination phase. If pure CO₂ is to be produced in a commercial process, a high-CO₂ calcination atmosphere must be used along with a higher calcination temperature. These tests confirmed that the optimal carbonation temperature was in the 60°C to 70°C range. The minimum temperature is established by the dew point of the feed gas while the maximum temperature is limited by the thermodynamics of the reversible carbonation reaction. The carbonation rate was found to increase with increases in both the H₂O and CO₂ concentrations.

The addition of SO₂ (0.1% to 0.4%) to the carbonation feed gas to simulate the flue gas composition from combustion of a sulfur-containing fuel produced a rapid decrease in CO₂ removal capacity due to the formation of Na₂SO₃. For example, when 0.1% SO₂ was added to the feed gas, the sorbent capacity for CO₂ removal decreased by about 76% during five-cycle tests. The Na₂SO₃ was stable in an inert atmosphere at temperatures as high as 200°C. When sulfur-containing fossil fuels are used, the CO₂ sorbent capture step must be downstream of a desulfurization step.

Fixed-bed reactor tests with product gas analysis as a function of time using gas chromatography were used to study the extent of CO₂ removal as a function of time. Nominal carbonation temperatures of 60°C and 70°C were studied, along with calcination in N₂ at 120°C and in CO₂ at both 160°C and 200°C. Five-cycle tests and one 15-cycle test were used to obtain additional information on sorbent durability. When the fixed-bed tests were carried to completion, the final percentage conversion of Na₂CO₃ to Wegscheider's salt was approximately 100% in the 60°C tests and about 90% in the tests at 70°C.

Fluidized-bed reactor tests of up to five cycles were conducted. Carbonation of sodium carbonate in these tests was initially very rapid and high degrees of removal were obtained. The exothermic nature of the carbonation reaction resulted in a rise in bed temperature and subsequent decline in removal rate. Good temperature control, possibly through water addition and subsequent evaporative cooling, appears to be the key to getting consistent carbon dioxide removal in a full-scale reactor system.

The tendency of the alkali carbonate sorbents to cake on contact with liquid water complicates laboratory investigations as well as the design of larger scale systems. The low temperature range in which the carbonation reaction takes place is suited to treatment of coal-derived flue gases following wet flue gas desulfurization processes, but limits the concentration of water vapor which is an essential reactant in the carbonation reaction. Also these sorbents have low attrition resistance and cannot be used without modification in dilute-phase transport reactor systems.

Sodium and potassium carbonate have been incorporated in high surface area ceramic supports to obtain greater surface area and attrition resistance, using a laboratory spray dryer. The caking tendency is reduced and attrition resistance increased by supporting the sorbent. Supported sorbents with loadings of up to 40 wt% sodium and potassium carbonates have been prepared and tested. These materials may improve the feasibility of large-scale CO₂ capture systems based on short residence time dilute-phase transport reactor systems.

CHAPTER 1

INTRODUCTION

Global warming, increasingly thought to be associated with the atmospheric emission of greenhouse gases, principally CO₂, is emerging as the key environmental issue of the early 21st century. The average atmospheric concentration of CO₂ has increased from 280 ppm to 370 ppm during the last 150 years, or since the beginning of the industrial revolution. During that same period, the average global temperature has increased by as much as 1°C (Berger, 2002). Continued uncontrolled emission of greenhouse gases may lead to increases in sea levels and increased frequency and intensity of climatic extremes such as hurricanes and floods.

Fossil fuels used for power generation, transportation, and by industry are the primary sources of anthropogenic CO₂ emissions to the atmosphere. While there are many potential approaches to limiting greenhouse gas emissions, including increased energy efficiency and use of carbon-free or low-carbon fuels, it is becoming increasingly clear that CO₂ capture and sequestration must play an important role in attacking the global warming problem. Initial CO₂ capture effort will no doubt focus on large stationary sources, with fossil fuel-fired power plants being obvious prime targets. New technologies including O₂ combustion with CO₂ recycle (Douglas et al., 2003), pre-combustion decarbonization (Doctor et al., 2001), and chemical looping combustion (Hurst et al., 2003; Yu et al., 2003) are under development. These technologies, in addition to being expensive and energy intensive, cannot generally be retrofitted to the large number of existing power plants.

The only currently available process for capturing CO₂ from flue gas that is also capable of being retrofitted to existing plants is based on amine scrubbing. For example, the Econamine FG Plus process (Reddy et al., 2003), which uses a solvent of monoethanolamine with an oxidation inhibitor, has been used commercially in a number of plants for CO₂ recovery. Amine-based scrubbing processes, however, are costly and energy intensive because of the large volume of gas to be treated, the low partial pressure of CO₂ in the flue gas, the presence of contaminants that may be detrimental to the solvent, and the energy demand associated with solvent regeneration.

This study is based on the use of a dry, regenerable, alkali carbonate-based sorbent to remove CO₂ from flue gases. Sorbent regeneration produces a gas stream containing only CO₂ and H₂O. Condensation of H₂O produces a pure CO₂ stream suitable for subsequent use or

sequestration. The work described in this report primarily involved sodium carbonate as the active component of the sorbent.

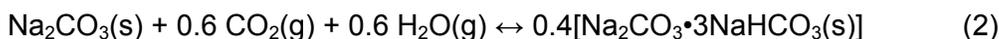
This topical report describes work conducted under a cooperative agreement with the U.S. Department of Energy by RTI International, LSU, and Church and Dwight, Inc.

1.1 PROCESS CHEMISTRY

The important reactions involved in the capture of CO₂ using sodium carbonate (Na₂CO₃) sorbent result in the reversible formation of sodium bicarbonate (NaHCO₃) and Wegscheider's salt (Na₂CO₃•3NaHCO₃):



$$\Delta H_r^\circ = -32.4 \text{ kcal/mol CO}_2$$



$$\Delta H_r^\circ = -32.5 \text{ kcal/mol CO}_2$$

Several patents (Krieg et al., 1984; Sarapata et al., 1987; and Falotico, 1993) describe processes and process improvements to optimize Reaction 1. Both forward reactions are exothermic; energy management will be an important consideration in a commercial system. Other potential reaction products such as sodium sesquicarbonate, Na₂CO₃•NaHCO₃•2H₂O, and sodium bicarbonate hydrate, NaHCO₃•2H₂O, were found to be of negligible importance at reaction conditions of interest.

Phase diagrams supplied by Church and Dwight, Inc. (Church and Dwight, 2000), indicate that Wegscheider's salt is favored at reaction conditions of 70°C and above at the H₂O and CO₂ partial pressures studied. X-ray diffraction analysis of the product from a fixed-bed reactor test at a nominal temperature of 70°C confirmed the formation of Wegscheider's salt.

Trona (a naturally occurring mineral used for production of soda ash) may be used to produce a regenerable sorbent for CO₂ according to the following reactions:

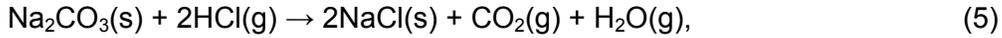
Trona is initially calcined according to



Subsequent carbonation and calcination reactions proceed according to



Potential contaminants in flue gas, such as SO₂ and HCl, will react irreversibly with Na₂CO₃ and must be reduced to low levels prior to CO₂ capture. HCl and SO₂ in the flue gas are also absorbed by Na₂CO₃ according to the following reactions:



Reactions 5 and 6 are not reversible under the conditions expected for regenerable capture of CO₂.

1.2 INDUSTRIAL APPLICATION

A process based on the chemistry described above could be retrofitted into existing power plants or installed in new plants. A conceptual process employing fast fluidized-bed reactors for carbonation and regeneration of sorbent is shown in Figure 1.

The technical feasibility of such a process depends on rapid reaction rates and long sorbent life. Important economic factors include the use of low-value heat from the power plant for sorbent regeneration and efficient movement of sorbent.

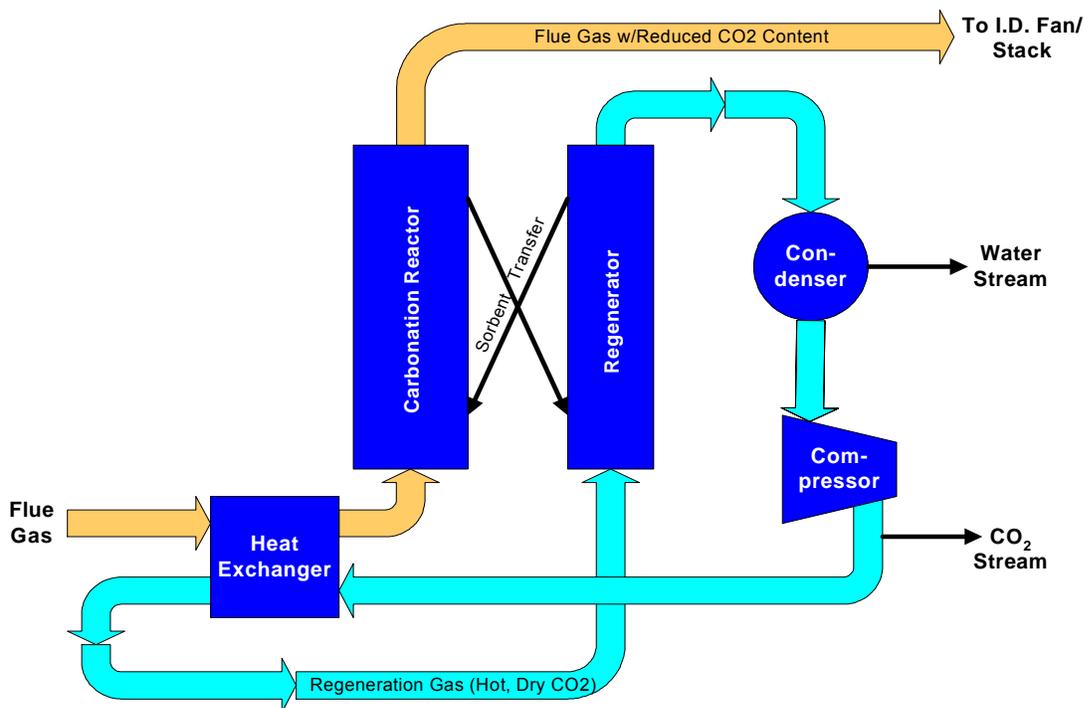


Figure 1. Conceptual carbon dioxide capture process using regenerable sorbent

CHAPTER 2

EXPERIMENTAL

2.1 ELECTROBALANCE EXPERIMENTS CONDUCTED AT LSU

2.1.1 Apparatus

The electrobalance reactor (or thermogravimetric analyzer [TGA]) monitors the change in weight associated with reaction as a function of time, temperature, and feed gas composition, but provides no information on CO₂ removal efficiency. A schematic diagram of the electrobalance reactor system, which consists of a gas flow system, a Cahn model 2000 electrobalance, a MicRICON temperature programmer-controller, and a personal computer (PC) for data acquisition and storage, is shown in Figure 2. Pure He and CO₂ were obtained from high-pressure cylinders and their flow rates were monitored using calibrated rotameters equipped with needle valves. Helium was used as the inert gas instead of N₂ to reduce aerodynamic noise and increase electrobalance sensitivity. H₂O was fed as a liquid using a positive displacement syringe pump. Feed lines were heat traced to insure complete vaporization of the H₂O. The He flow was split with a portion introduced at the top of the system to protect the electrobalance mechanism from corrosive reactive gases. The remaining He, mixed with CO₂ and steam, was fed to the electrobalance side arm, and the combined gases flowed downward over the reacting solid. The solid was held in a quartz cup and suspended from the electrobalance using a Pt wire. Temperature was monitored and controlled from a chromel-alumel thermocouple positioned approximately ¼-inch below the sample in the isothermal zone.

2.1.2 Electrobalance Reaction Conditions

The effects of calcination and carbonation temperature and calcination and carbonation gas composition were examined in the electrobalance tests. In addition, multicycle tests were carried out to obtain preliminary data on sorbent durability. Six sorbents were tested, but the extent of testing varied between the sorbents. Calcination temperature was varied between 120°C and 200°C while most calcination tests used an atmosphere of pure He. The He atmosphere is not realistic from a commercial viewpoint, but was chosen to minimize the severity of sorbent exposure during the calcination phase. Additional calcination tests were carried out in more realistic conditions using pure CO₂ and in a mixture of 80% CO₂-20% H₂O. However, the increased CO₂ partial pressure required a higher calcination temperature.

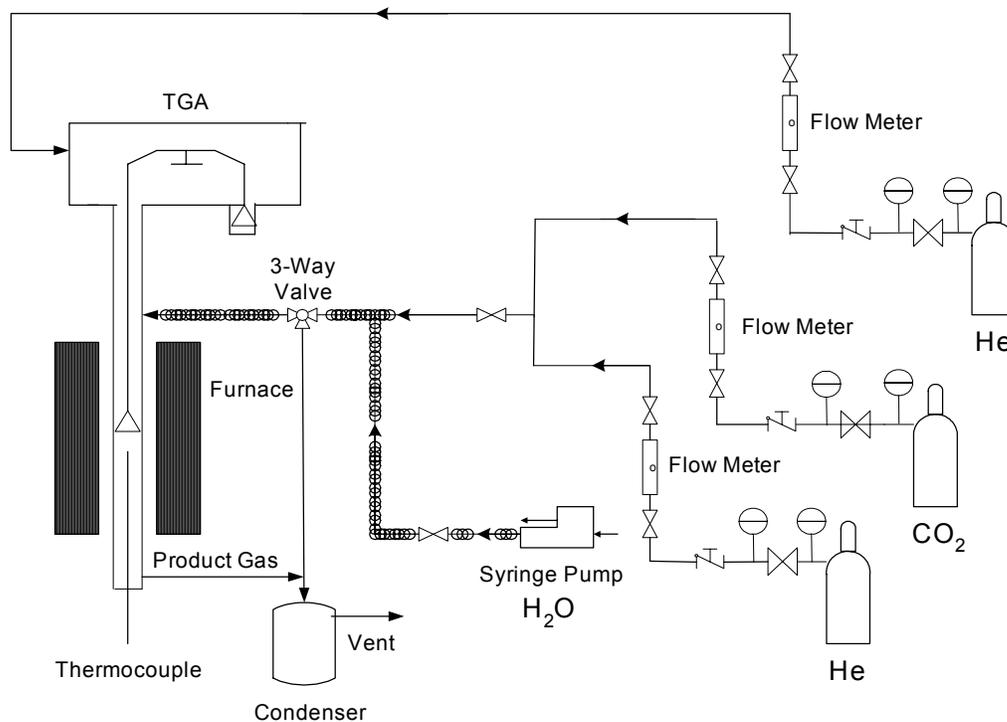


Figure 2. Schematic of the electrobalance reactor system

Carbonation temperature was varied between 60°C and 80°C and most carbonation tests used a standard feed composition of 8% CO₂, 16% H₂O, and 76% He (all mol %). With the exception of the substitution of He for N₂ and the absence of excess O₂, this composition approximates that of flue gas obtained when natural gas is completely combusted in 10% excess air. In selected tests the CO₂ and H₂O concentrations were varied to determine the effect of these gas concentrations. Carbonation product was considered to be NaHCO₃ in tests conducted at 60°C, and Wegscheider's salt in tests at 70°C and 80°C.

2.1.3 Typical Electrobalance Test Result

Results of a typical single-cycle electrobalance test using sorbent SBC#3 are shown in Figure 3 where dimensionless weight and temperature are plotted versus time. Approximately 70 mg of sorbent precursor was heated from ambient to 100°C at a rate of 5°C/min, and then to 120°C at 1°C/min under flowing He. Calcination of NaHCO₃ to Na₂CO₃ began at about 100°C and was complete soon after the temperature reached 120°C. The final experimental dimensionless weight was quite near the theoretical value of 0.631 that is indicated by the horizontal dashed

line in the figure. The system was then cooled to the carbonation temperature under flowing He and, after about 190 min, the gas composition was changed to 8% CO₂, 16% H₂O, and 76% He flowing at 600 sccm. The subsequent increase in dimensionless weight corresponded to the carbonation of Na₂CO₃ and removal of CO₂ from the gas phase. The global carbonation rate was rapid initially and decreased as the reaction approached completion. The final dimensionless weight of 0.84 was quite near the theoretical value of 0.85 corresponding to the complete conversion of Na₂CO₃ to Wegscheider's salt.

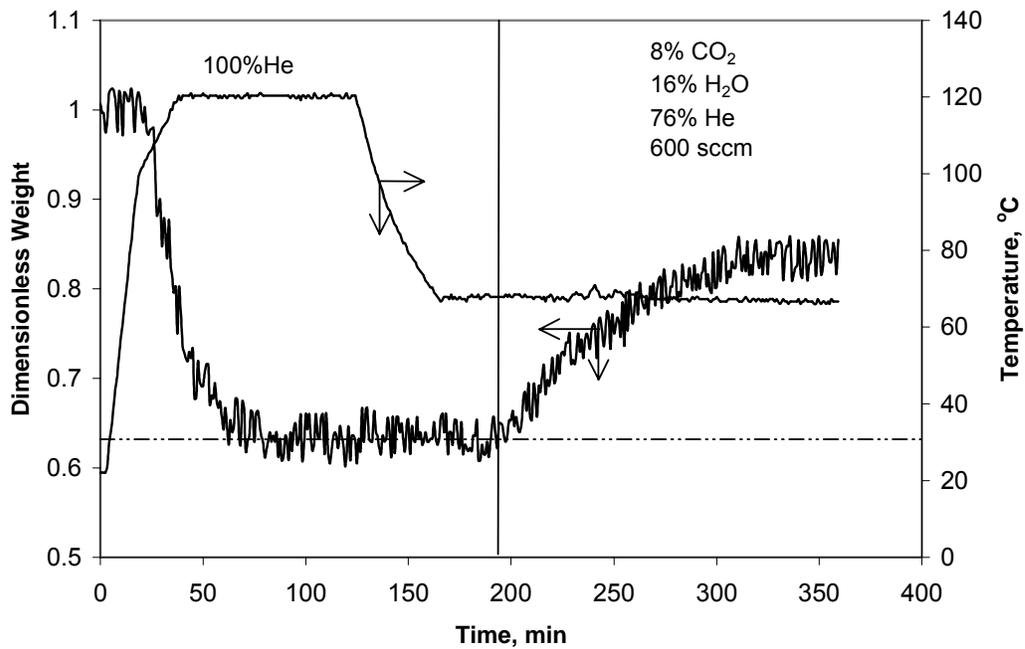


Figure 3. Typical results from a single-cycle electrobalance test (SBC#3)

Calcination of both the SBC and trona samples was complete in all of the electrobalance tests presented in this report. Many of the carbonation results that follow are presented as fractional carbonation at selected times. The equations for calculating fractional carbonation depend on both the composition of the precursor and whether the carbonation product is Na₂CO₃ or Wegscheider's salt. The following equations have been used.

SBC Precursor – Na₂CO₃ Product

$$f(t) = \frac{w(t) - 0.631}{0.369} \quad (7)$$

SBC Precursor – Wegscheider’s Salt Product

$$f(t) = \frac{w(t) - 0.631}{0.221} \quad (8)$$

Trona T-50 Precursor – Na₂CO₃ Product

$$f(t) = \frac{w(t) - 0.723}{0.385} \quad (9)$$

Trona T-50 Precursor – Wegscheider’s Salt Product

$$f(t) = \frac{w(t) - 0.723}{0.231} \quad (10)$$

Trona T-200 Precursor – Na₂CO₃ Product

$$f(t) = \frac{w(t) - 0.711}{0.401} \quad (11)$$

Trona T-200 Precursor – Wegscheider’s Salt Product

$$f(t) = \frac{w(t) - 0.711}{0.241} \quad (12)$$

In equations 4 through 9, $f(t)$ is the fractional carbonation at time t , and $w(t)$ is the dimensionless weight at time t . 0.631, 0.723, and 0.711 are the dimensionless weights corresponding to complete calcination of the SBC samples, trona T-50, and trona T-200, respectively. 0.369, 0.385, and 0.401 are the dimensionless weight increases associated with complete conversion of the calcined product to NaHCO₃ for the SBC samples, trona T-50, and trona T-200, respectively. Finally, 0.221, 0.231, and 0.241 are the dimensionless weight increases associated with complete conversion of the calcined product to Wegscheider’s salt for the SBC samples, trona T-50, and trona T-200, respectively. These equations are based on the assumption that the inert materials in trona T-50 and trona T-200 are nonvolatile.

2.2 THE FIXED-BED REACTOR LSU

2.2.1 Apparatus

The fixed-bed reactor system, shown in Figure 4, also consisted of a gas flow system, the fixed-bed reactor, a temperature programmer-controller connected to a single-zone split-tube furnace, and a Shimadzu Model GC-14A gas chromatograph. Pure CO₂ and, in this case, inert N₂ were obtained from high-pressure cylinders, with flow rates controlled by mass flow controllers. In early tests, as shown in Figure 3, H₂O was added as a liquid using a syringe pump, and the feed

lines were heat traced to insure complete vaporization. In later tests the syringe pump was replaced and H₂O was added by bubbling N₂ and CO₂ gases through H₂O contained in a temperature-controlled wash bottle. The exit gases were assumed to be saturated with H₂O. The narrow window between the temperature needed to vaporize the H₂O and the desired reaction temperature prompted this change. With too much preheat added to the H₂O line from the syringe pump, the combined gas temperature exceeded the desired reaction temperature. With too little preheat, not all of the H₂O vaporized. Control proved to be easier using the gas bubbler and the quality of data improved after the change was made.

Combined gases entered near the bottom of the reactor vessel, and the gases were preheated to reaction temperature as they flowed upward in the annular space between the vessel and reactor insert. The gases then flowed downward through the fixed bed of sorbent, which was supported using a porous stainless disc. Thin layers of quartz wool were placed between the porous disc and sorbent and also above the sorbent. Product gases exited from the bottom of the reactor vessel into a condenser for removal of excess H₂O, and then passed to the gas chromatograph for analysis.

The gas chromatograph, equipped with an automatic 10-port sampling valve, dual columns, methanizer, and both thermal conductivity detectors (TCDs) and flame ionization detectors (FIDs), was used to determine the CO₂ concentration in the product gas as a function of time. Product gases from the condenser first entered a HayeSep-N column to trap trace quantities of moisture that escaped the condenser. CO₂ was then separated from the dry gases using a Carboxen 1000 column while the HayeSep column was backflushed to vent. The carrier gas was UHP N₂. Gases eluted from the Carboxen column flowed first to the TCD, then to the methanizer where CO₂ was converted to CH₄, and finally to the FID where the CO₂ concentration was determined.

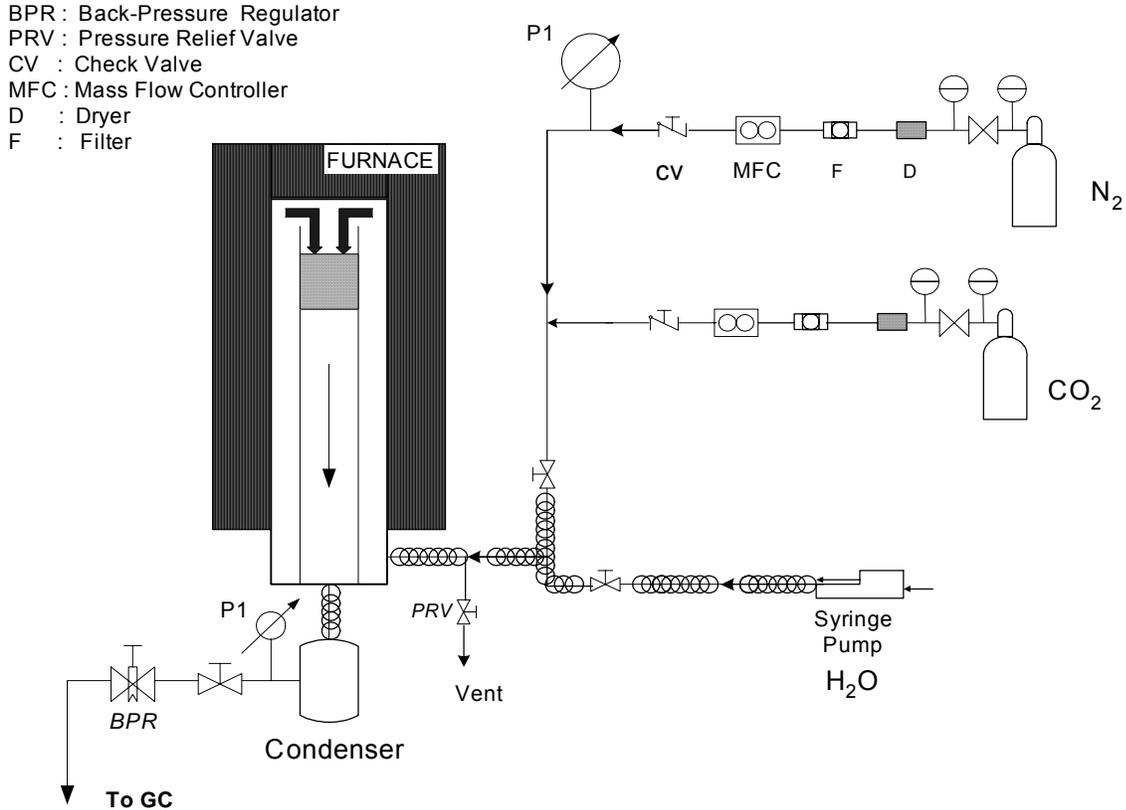


Figure 4. Schematic of the fixed-bed reactor system

2.2.2 Fixed-Bed Reaction Conditions

The standard carbonation gas composition of 8% CO₂, 16% H₂O, and 76% N₂ was used in all tests. N₂ was substituted for He as aerodynamic noise and balance sensitivity were no longer of concern. As with the electrobalance tests, carbonation temperature was varied between nominal temperatures of 60°C and 80°C. Nominal temperatures were reported in all fixed-bed reactor tests, as the energy released by the exothermic carbonation reaction was sufficient to increase the bed temperature above the nominal setting. The carbonation product was considered to be Wegscheider's salt in all fixed-bed tests because of the increase in temperature above the nominal setting. Once again, calcination temperature was varied between 120°C and 200°C and either pure He or pure CO₂ was used as the calcination atmosphere. Sorbent SBC#3 was used in most of the fixed-bed tests, and multicycle testing was emphasized. In the fixed-bed reactor tests, product gas composition was analyzed by gas chromatography to determine CO₂ removal efficiency.

2.2.3 Typical Fixed-Bed Test Result

Typical results from a two-cycle fixed-bed reactor test using SBC#3 are shown in Figure 5. CO₂ concentration (dry basis) and nominal reaction temperature are plotted as a function of time. In this test, the first calcination was carried out in N₂ at 120°C during day 1 and the reactor was allowed to cool overnight in flowing N₂ to the desired carbonation temperature. The first carbonation and second calcination were completed during day 2. Carbonation occurred at a nominal 60°C in a feed gas containing 8% CO₂, 16% H₂, and 76% N₂; second-cycle calcination conditions were the same as in cycle 1. Finally, the second carbonation was completed during day 3 using the same conditions as in carbonation Cycle 1.

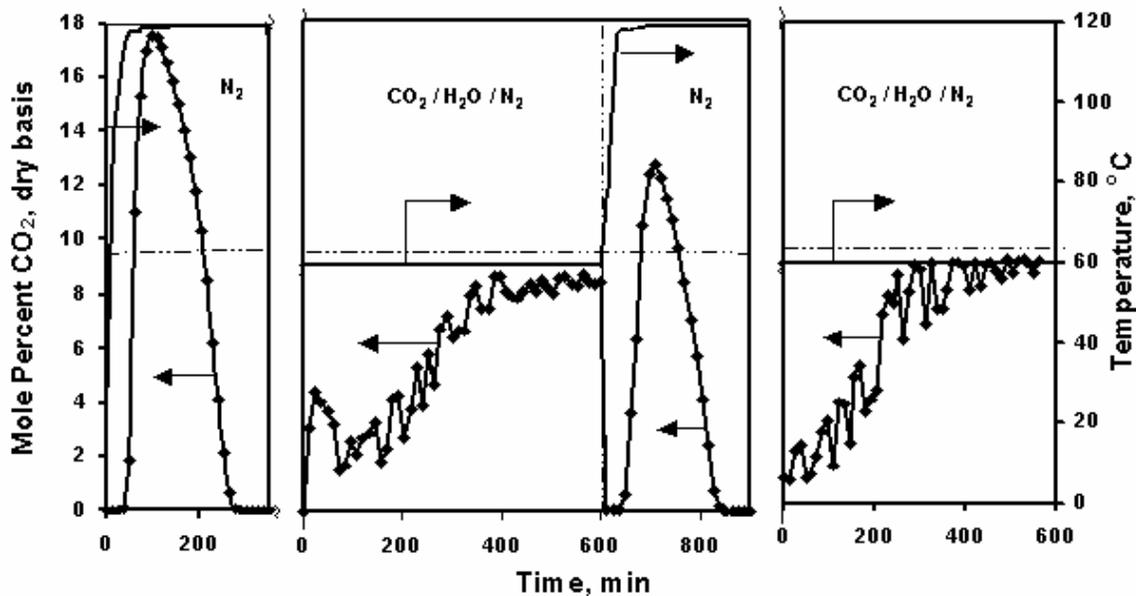


Figure 5. Typical results from a two-cycle fixed-bed reactor test (SBC#3)

CO₂ was first detected in calcination Cycle 1 at about 100°C, reached a maximum concentration of almost 18% in just over 100 min, and then decreased to zero by 300 min, indicating that calcination was complete. Good material balance closure was obtained with numerical integration of the area under the concentration-time curve showing that 0.159 mols of CO₂ were produced, compared to the stoichiometric amount of 0.159 mols based on the mass of the initial Na₂CO₃ charge. Initial CO₂ concentration during the first carbonation cycle was almost 5%, corresponding to about 50% CO₂ removal. The CO₂ concentration then decreased to just over 1% before increasing monotonically in a standard breakthrough curve. 1% CO₂ (dry basis) in the product gas corresponds to about 90% CO₂ removal. During the second calcination cycle, the maximum CO₂ concentration was about 13%, and the area under the curve corresponded to

0.089 mols of CO₂. While this amount was 58% less than the amount liberated during the first calcination, it corresponded to greater than 90% conversion of Na₂CO₃ to Wegscheider's salt. Initial CO₂ concentration during the second carbonation cycle was about 1% and the concentration increased monotonically throughout the carbonation test. The CO₂ concentration decrease that occurred early in the first carbonation cycle and was not repeated during the second cycle was a general trend noted in several of the multicycle fixed-bed tests. This can be attributed to rearrangement of the packed bed, which minimized gas bypassing.

2.3 FLUIDIZED-BED EXPERIMENTS AT RTI

RTI conducted six cyclic fluidized-bed tests in a 2-inch diameter bench-scale system. SBC, trona, potassium carbonate, and two different supported sorbents were tested. The reactor system is shown in Figure 6. The reactant gas supply consists of three electronic mass flow controllers (MFCs) which are used to meter nitrogen, air, and carbon dioxide from compressed gas cylinders. These MFCs were calibrated against a soap bubble flow meter. Deionized water was added to the mixed dry gas stream using a high-pressure liquid chromatography (HPLC) pump. The reactor consists of a 2-inch internal diameter quartz tube, fitted with a 3-mm thick porous quartz plate distributor. The reactor is suspended within a flanged 4-inch stainless steel pipe that is surrounded by a three-zone electric furnace. Inlet gas enters the top flange of the pipe, passes through the annulus, and enters the quartz reactor through the distributor at the bottom. A 6-inch bed of sorbent (or sorbent precursor) is initially charged to the reactor to maintain a length-to-diameter ratio of 3. Effluent gas passes through a shell and tube heat exchanger for condensation of steam, a Hartmann and a Braun Model URAS-14 nondispersive infrared carbon dioxide monitor. The sorbent bed contains 3 Type-K thermocouples spaced at 1, 3, and 5 inches above the distributor. An electronic differential pressure gauge connected with a digital display indicates the pressure drop across the bed. Total pressure is also monitored.

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

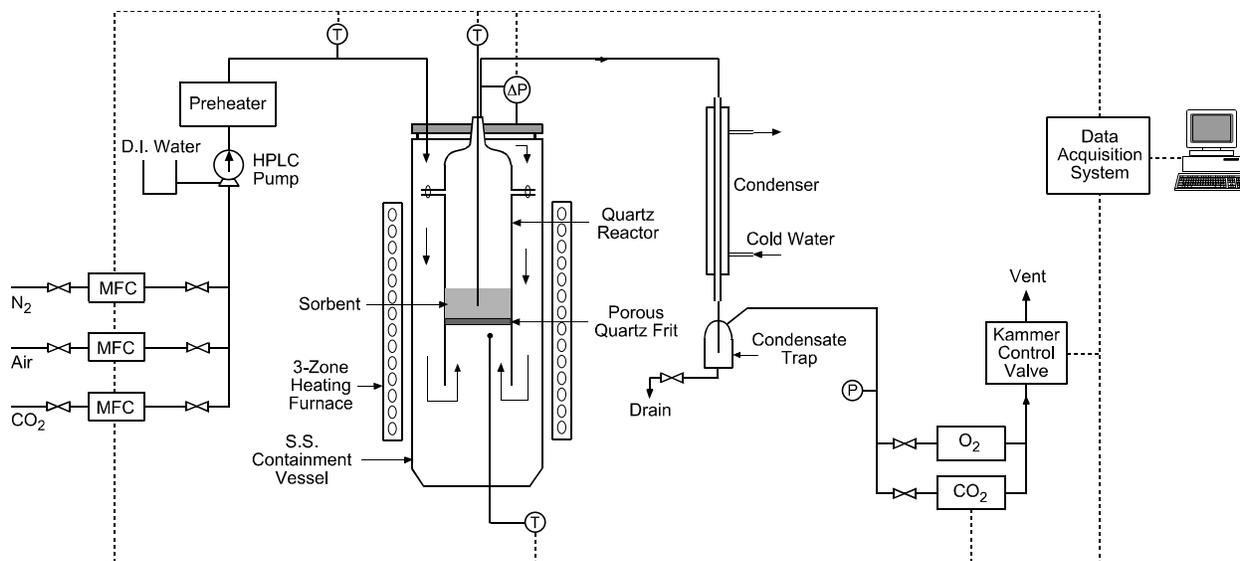


Figure 6. Fluidized-bed test reactor system

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. This equipment modification was attempted between the second and third 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 the addition of deionized water. This modification was removed as it proved to be unworkable because the sorbent caked and plugged the bed upon exposure to liquid water.

2.4 DETERMINATION OF PHYSICAL PROPERTIES OF SORBENTS

2.4.1 Particle Size Determinations

Particle size distributions were measured using a sieve shaker apparatus and a Sympatec-Helos laser diffraction analyzer.

2.4.2 BET Measurements

Brunauer-Emmett-Teller (BET) surface area determinations were conducted with a Quantachrome Nova 1000 instrument. The Nova 1000, shown schematically in Figure 7, has a pore diameter range of 3.5 to 2000 Å and an accuracy of 0.1 percent. The minimum resolvable

pressure is 0.016 torr. Determinations on various grades of SBC were conducted as received and after overnight calcination at 125°C (257°F). In addition, some samples were tested after shorter calcination periods. The outgassing temperature for all determinations was 250°C (482°F).

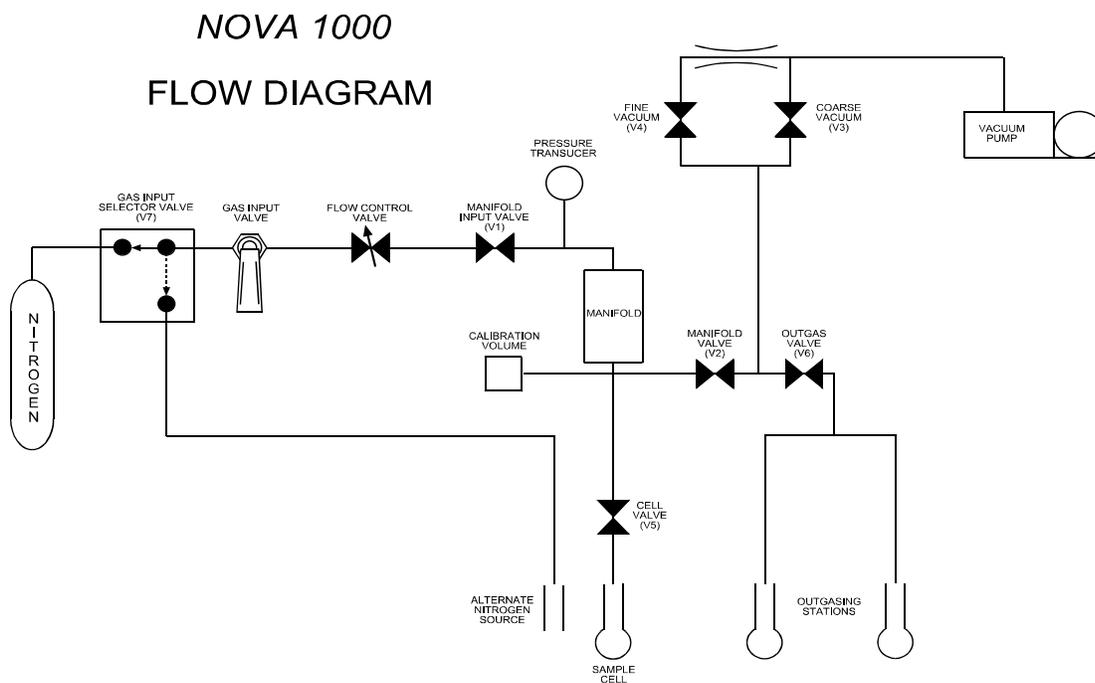


Figure 7. NOVA 1000 flow diagram

2.4.3 Porosimetry

Mercury porosimetry determinations were conducted with a Micromeritics AutoPore II 9220 instrument coupled to a PC equipped with AutoPore II software, version 3.01. Triple distilled mercury was used for all determinations. Measurement of pore volume, pore volume distribution, and median pore diameter by mercury intrusion provides a direct indication of diffusional resistance associated with the sorbents. Determinations were conducted on materials as received, and after calcination overnight at 125°C (257°F).

2.4.4 Attrition

Attrition measurements of unsupported sorbents were made using a 3-hole air-jet attrition tester using the ASTM D 5757-95 method. Attrition measurements of supported sorbents were made using a "Davison type" jet cup apparatus that is typically used in industry for measuring attrition of a fluidized catalytic cracking (FCC) catalyst. A generic description of the jet cup apparatus

and the procedure used has been published (Zhao et al., 2000). To remove apparatus-related bias the jet cup attrition values of the samples tested are reported as attrition ratio, where attrition ratio (AR) is defined as:

$$AR = \frac{\text{Jet cup attrition index of the sample}}{\text{Jet cup attrition index of a standard}}$$

The standard chosen for these tests is an equilibrium FCC catalyst, that is known to be a relatively attrition resistant material. Based on the above equation, the higher the AR, the higher is the sample likely to undergo attrition in a fluidized-bed or transport reactor.

2.5 PREPARATION OF SUPPORTED SORBENTS

RTI prepared sorbents composed of up to 40% sodium carbonate on alumina-type support materials. The bulk of these materials were prepared using a laboratory-scale spray dryer with a capacity of 1 to 2 kg/day. One spray-dried sorbent prepared in the laboratory was successfully scaled up to a 200 kg batch by a commercial catalyst manufacturer. The supported sorbents were subjected to reactivity screening analyses by thermogravimetric analysis at RTI. Selected samples were also subjected to surface area and attrition determinations.

CHAPTER 3

RESULTS

3.1 SINGLE CYCLE ELECTROBALANCE TESTING AT LSU

The electrobalance was used to compare performance of the different sorbent precursors and to evaluate the effects of calcination and carbonation temperature and gas composition on sorbent performance. The effect of calcination conditions was evaluated by comparing performance in the subsequent carbonation cycle, particularly in multicycle tests where sorbent durability was studied. While six of the sorbent precursors were tested during early stages of the experimental program, SBC#3 received primary emphasis.

3.1.1 Reproducibility

The levels of reproducibility obtained from multiple tests at duplicate reaction conditions for SBC#3 and trona T-50 are shown in Figures 8 and 9, respectively. Dimensionless weight during the carbonation phase is plotted versus time. Separate samples of sorbent precursor were used in each of the six tests, and calcination occurred at 120°C in He. Calcination was complete in each test as indicated by the fact that the initial dimensionless weights were all equal to the theoretical values for calcination of NaHCO_3 and trona, respectively, represented by the horizontal dashed lines. Carbonation conditions were identical in each of the six tests and are shown on the figures. The raw electrobalance data were smoothed so that results from individual tests could be identified.

SBC#3 results in Figure 8 showed a small variation in initial carbonation rate, but the overall results were quite reproducible. Final dimensionless weights in each case were 0.84, which corresponds to 95% carbonation to Wegscheider's salt product. Results from two of the trona T-50 tests in Figure 9 were quite similar, but there was a significant difference in the third test. The final dimensionless weights were 0.91 and 0.92, which correspond to 80% and 83% conversion to Wegscheider's salt.

The results shown in these figures were typical in that good reproducibility was normally achieved using all SBC precursors, while scatter even larger than shown in Figure 9 occurred in some of the trona reproducibility tests. The wider range of particle sizes and the possible variation in impurity levels from sample to sample were identified as potential causes of the lack of reproducibility. Indeed, sieving the trona and using narrower particle size ranges improved,

but did not eliminate, the variation. As a result of the reproducibility studies, the SBC samples received greater emphasis in subsequent experiments.

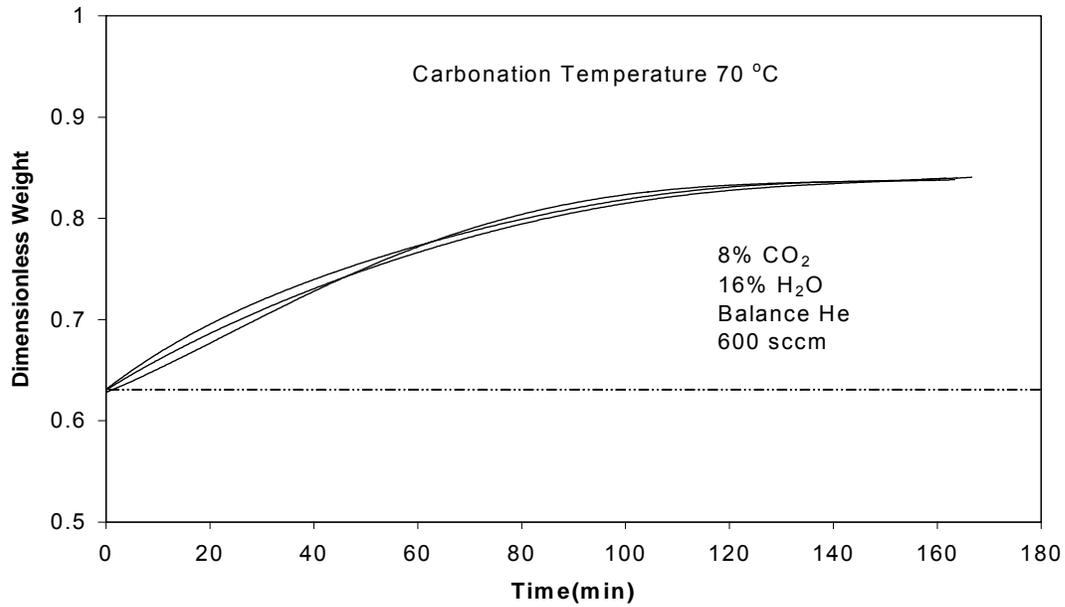


Figure 8. Duplicate carbonation test results using SBR#3

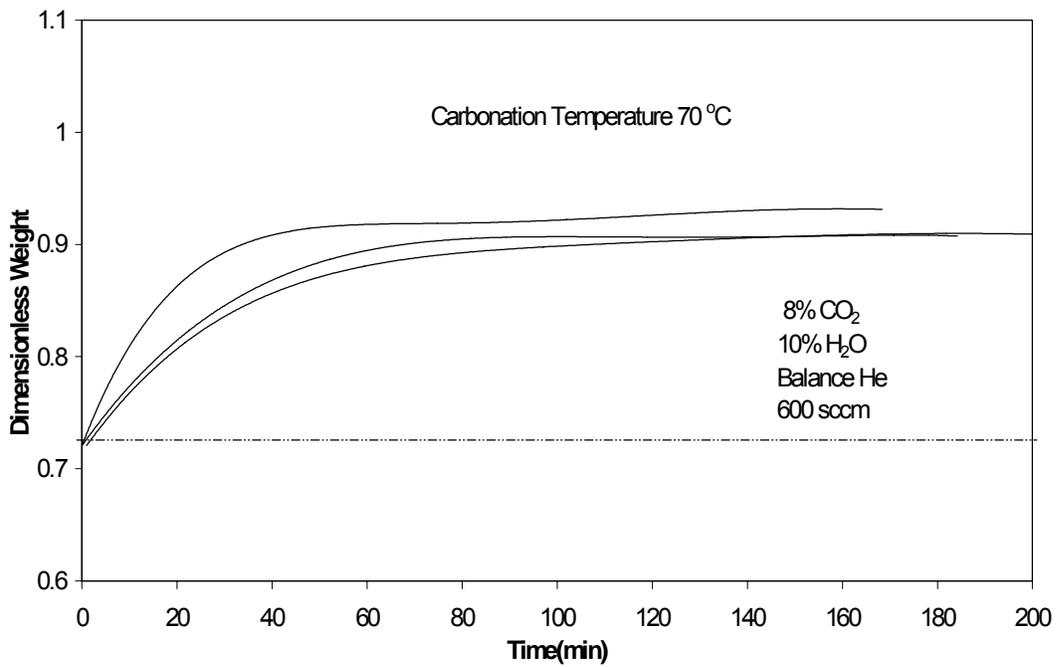


Figure 9. Duplicate Carbonation Test Results Using Trona T-50

3.1.2 The Effect of Carbonation Temperature

Temperature affects both the kinetics and thermodynamics of the carbonation reaction. Figure 10 compares smoothed electrobalance results for three tests using SBC#3 at carbonation temperatures of 60°C, 70°C, and 80°C. Calcination was carried out at 120°C in He and the carbonation gas contained 8% CO₂, 16% H₂O, and 76% He. Both the initial rate, as measured by the initial slope of the dimensionless weight-time curves, and the final dimensionless weight decreased with increasing temperature. The reaction rate approached zero after about 200 min at both 60°C and 70°C, but reaction was still occurring slowly at 80°C after 400 min.

Carbonation temperatures lower than 60°C are not practical, as the dew point of the feed gas is 56°C.

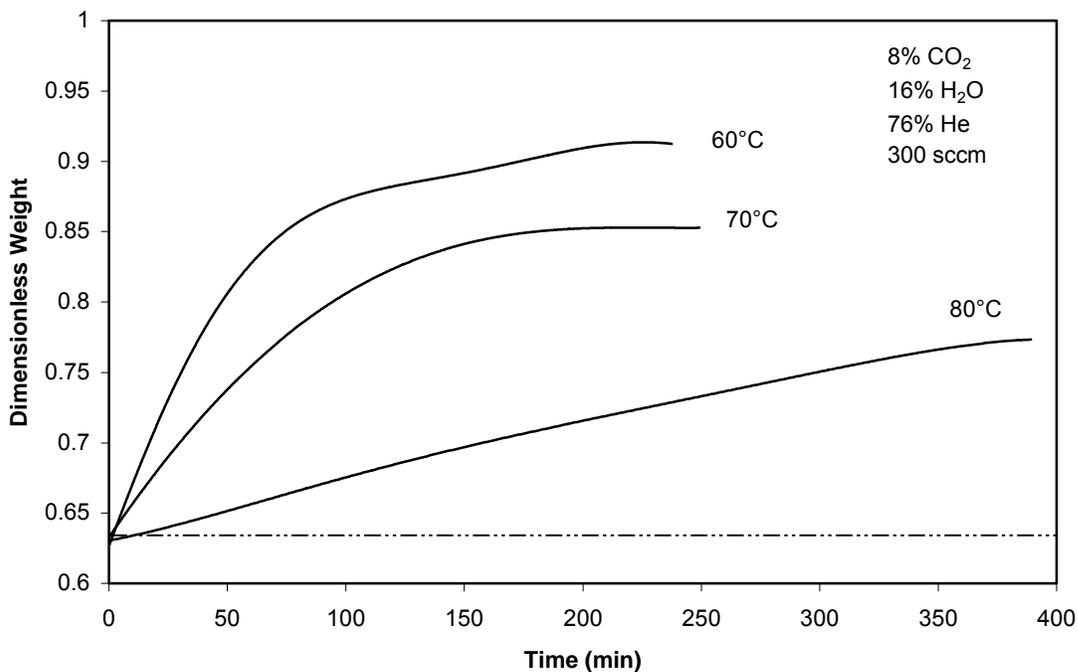


Figure 10. Effect of Temperature on the carbonation of SBC#3

The decrease in final dimensionless weight between 60°C and 70°C is attributed to the formation of different products – NaHCO₃ at 60°C and Wegscheider’s salt at 70°C. The final dimensionless weight of 0.92 at 60°C corresponds to 76% conversion of Na₂CO₃ to NaHCO₃, while the 0.84 final dimensionless weight at 70°C corresponds to about 95% conversion to Wegscheider’s salt. The decrease in rate between 70°C and 80°C is attributed to a decrease in concentration driving force due to the reversibility of the reaction. No reaction occurred at 80°C

when the CO₂ concentration was reduced to 5%, which is in agreement with thermodynamic calculations. These results emphasize the importance of careful temperature control because of the narrow temperature window available for CO₂ removal.

Somewhat different results were obtained when trona T-50 was tested at different temperatures as shown in Figure 11. The initial rate showed the exact opposite effect and decreased from 80°C to 70°C to 60°C. Final dimensionless weights at 70°C and 80°C were effectively equal at 0.92, while at 60°C the final weight was 0.98. These final dimensionless weights correspond to 85% conversion to Wegscheider's salt at 70°C and 80°C, and to 67% conversion to Na₂HCO₃ at 60°C. However, since different samples were used in each test, at least part of these effects may be due simply to the lack of reproducibility associated with trona carbonation.

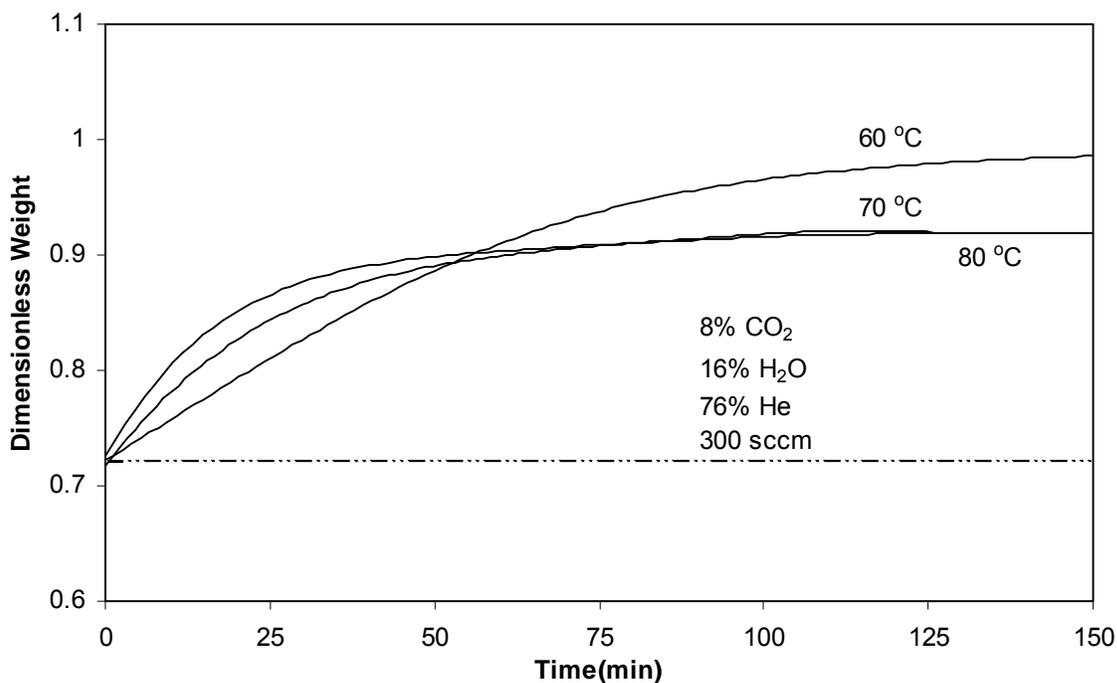


Figure 11. Effect of temperature on the carbonation of Trona T-50

3.1.3 Effect of CO₂ and H₂O Concentration

At a fixed carbonation temperature, increases in the concentration of both CO₂ and H₂O produced an increase in the carbonation rate, but little change in the final dimensionless weight. These effects are illustrated for SBC#3 in Figure 12 for CO₂ and Figure 13 for H₂O. When CO₂ was removed from the feed gas no reaction occurred, which confirmed that sodium carbonate

monohydrate, $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$, would not be formed at this temperature. Although the dimensionless weight after 250 min was slightly less in 5% CO_2 than in 8% CO_2 , reaction was still occurring at the lower concentration and extrapolation suggests that the final dimensionless weights would be approximately equal.

Changing the H_2O concentration had a similar effect as shown in Figure 13. The carbonation rate was clearly faster in 16% H_2O and the reaction was effectively complete in less than 200 min. Reaction was still occurring slowly after 400 min in 10% H_2O , but the final dimensionless weights were approximately equal.

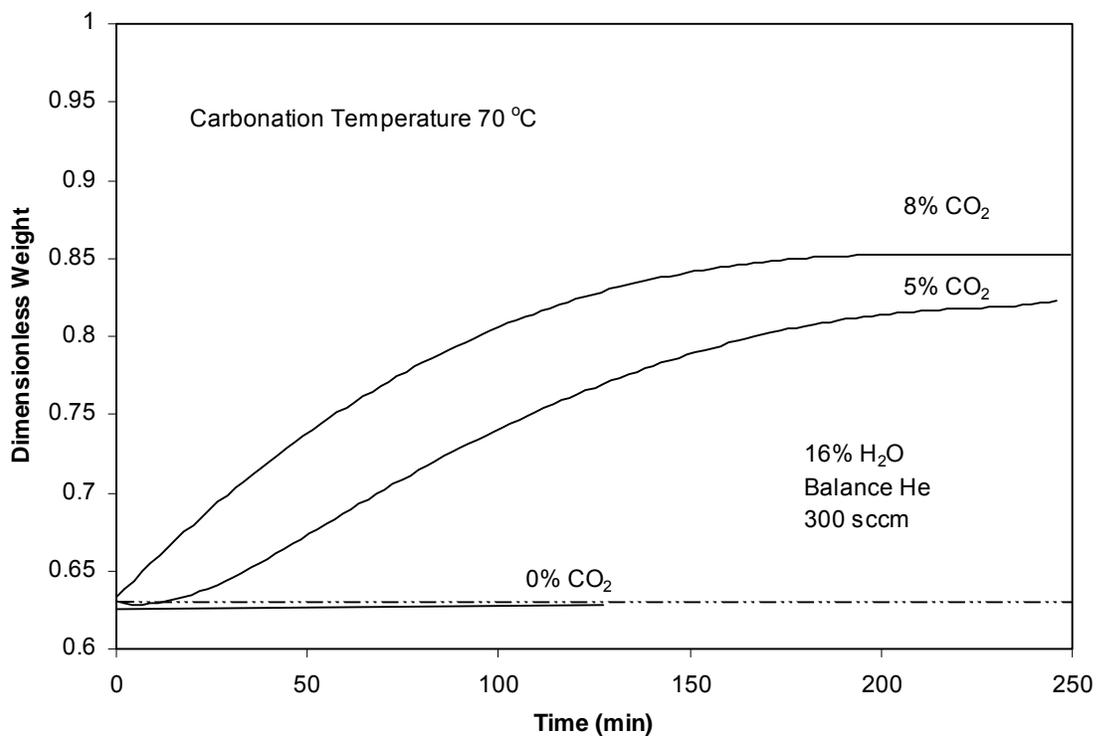


Figure 12. Effect of CO_2 concentration on the carbonation of SBC#3

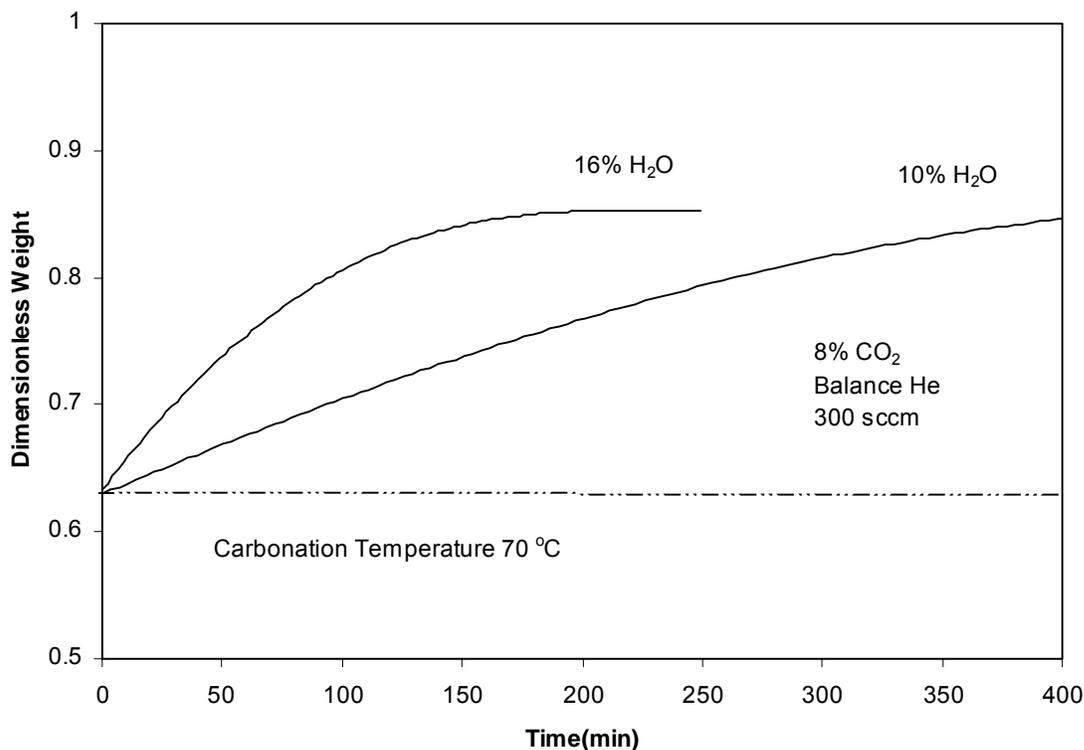


Figure 13. Effect of H₂O concentration on the carbonation of SBC#3

3.1.4 Comparison of Different Sorbents

Figure 14 compares the dimensionless weight versus time responses during the carbonation of three sorbents—SBC#1, SBC#3, and trona T-50—for a reaction temperature of 60°C, where the carbonation product should be NaHCO₃. The initial dimensionless weights are very close to the theoretical values of 0.631 for both SBC samples, as indicated by the lower horizontal line, and 0.723 for trona T-50, as indicated by the upper horizontal line. The initial reaction rates, which correspond to the initial slopes of the dimensionless weight-time curves, were approximately equal. The final dimensionless weights of the two SBC samples were also reasonably close, although SBC#1 took considerably longer to reach the final value. The final dimensionless weights of 0.94 for the SBC samples correspond to 83% conversion to NaHCO₃, while the final dimensionless weight of 0.99 for trona T-50 corresponds to only 69% conversion to NaHCO₃.

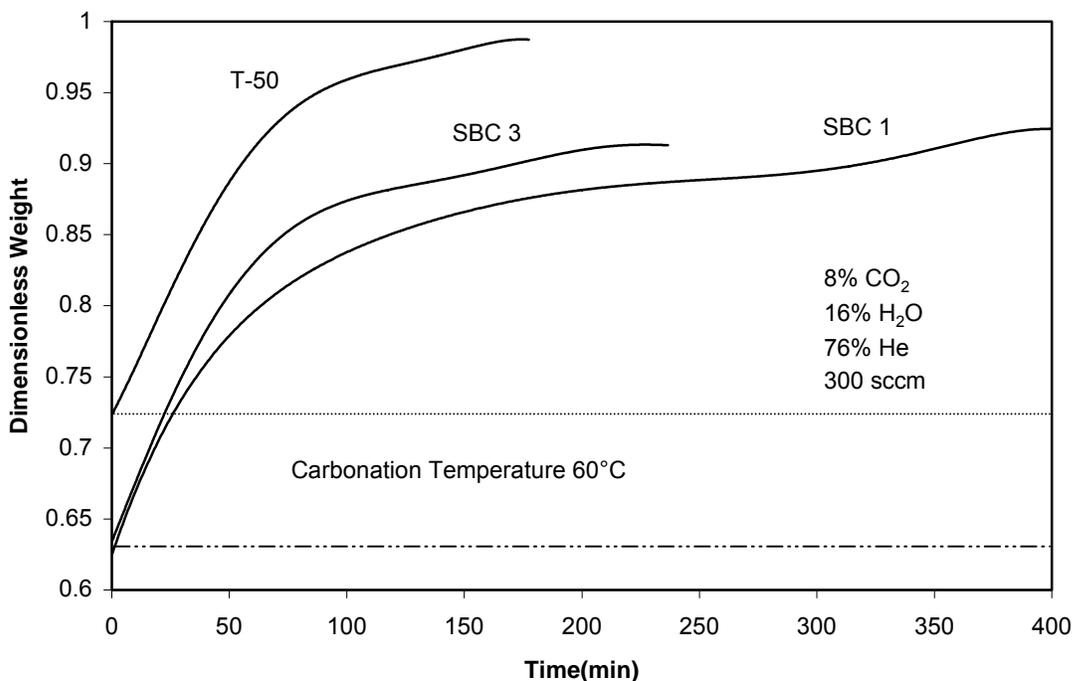


Figure 14. Comparison of the carbonation of three sorbents at identical carbonation conditions

3.1.5 Effect of Calcination Temperature and Atmosphere

In all the previous tests reported, the sorbent precursor was calcined at the mildest possible conditions in He at 120°C. In order to produce pure CO₂ during sorbent calcination, it will be necessary to carry out the calcination in an atmosphere containing a high concentration of CO₂, and the calcination temperature must be increased. The higher temperature will increase the possibility of sintering and cumulative loss of activity through many cycles. Results of carbonation tests in which calcination occurred in pure CO₂ at temperatures between 120°C and 200°C are shown in Figure 15; carbonation data following calcination in He at 120°C are included for comparison. Calcination results in pure CO₂ at 120°C are included, although the calcination rate at these conditions is too small to be of practical interest. On the basis of these single-cycle tests, it is clear that the more severe calcination conditions did not have an adverse impact on the subsequent carbonation. In fact, there was a slight increase in both the carbonation rate and the final dimensionless weight in each of the tests following CO₂ calcination compared to He calcination. Evaluation of possible cumulative effects requires multicyle tests.

3.2 MULTICYCLE ELECTROBALANCE TESTING AT LSU

Preliminary information on sorbent durability was acquired through a series of five-cycle tests. Carbonation conditions were constant in all cycles in all tests—70°C in 8% CO₂, 16% H₂O, and 76% He. Various sorbent precursors were tested and calcination temperature and atmosphere were varied. Durability was evaluated by comparing carbonation performance in each cycle.

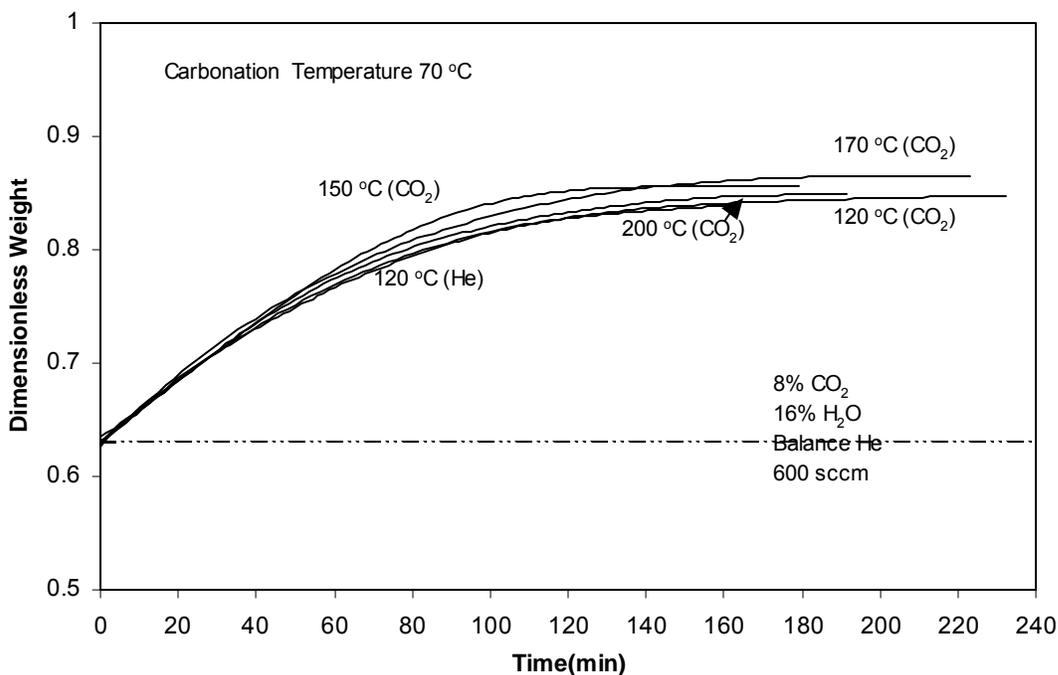


Figure 15. Effect of calcination atmosphere and temperature on carbonation kinetics (SBC#3)

3.2.1 Dimensionless Weight Versus Time Results

Raw electrobalance data from a five-cycle test using SBC#3 with calcination at 120°C in He are shown in Figure 16. Complete calcination, as indicated by the dimensionless weight of 0.63, was achieved at the end of all five calcination phases. The first carbonation was initiated after about 200 min and continued until the weight approached a constant value. The second calcination followed immediately. Then the sample was cooled to 70°C and left overnight in flowing He, with the second carbonation, third calcination, third carbonation, and fourth calcination carried out the next day. The fourth carbonation, fifth calcination, and fifth carbonation were completed on the third day. Thus, the time scale in Figure 16 is arbitrary following the first cycle.

Figure 16 clearly shows a decrease in the final dimensionless weight between carbonation Cycles 1 and 2 and again between Cycles 3 and 4. However, there was an increase in final dimensionless weight between Cycles 2 and 3 and no significant difference between Cycles 4 and 5. In addition, there was a small decrease in the slope of the dimensionless weight-time curves near the beginning of carbonation Cycles 1 and 2. Thereafter, the initial slopes were reasonably constant. These results are indicated more clearly in Figure 17 where smoothed electrobalance data during the five carbonation cycles are overlaid. Note that the maximum cycle time plotted in Figure 17 is 150 min, which is too short to show the larger final dimensionless weight in Cycle 3. However, Figure 14 also shows that carbonation is continuing after 150 min in Cycle 3, but has effectively stopped after 150 min in the other cycles. Both the reduced initial slope and reduced final dimensionless weight between Cycles 1 and 2 are clear.

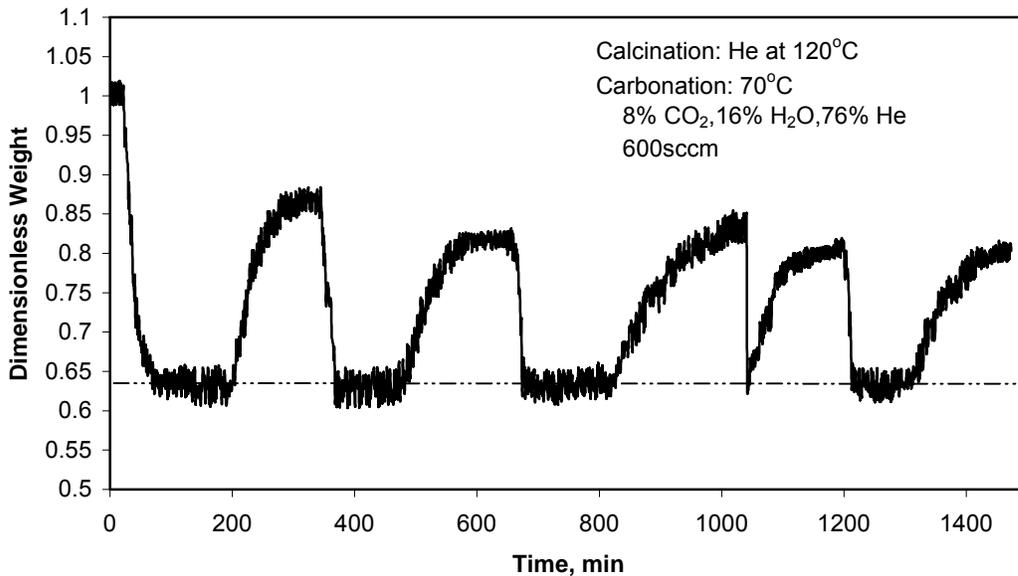


Figure 16. Raw electrobalance result from a five-cycle test using SBC#3: Calcination in He at 120°C

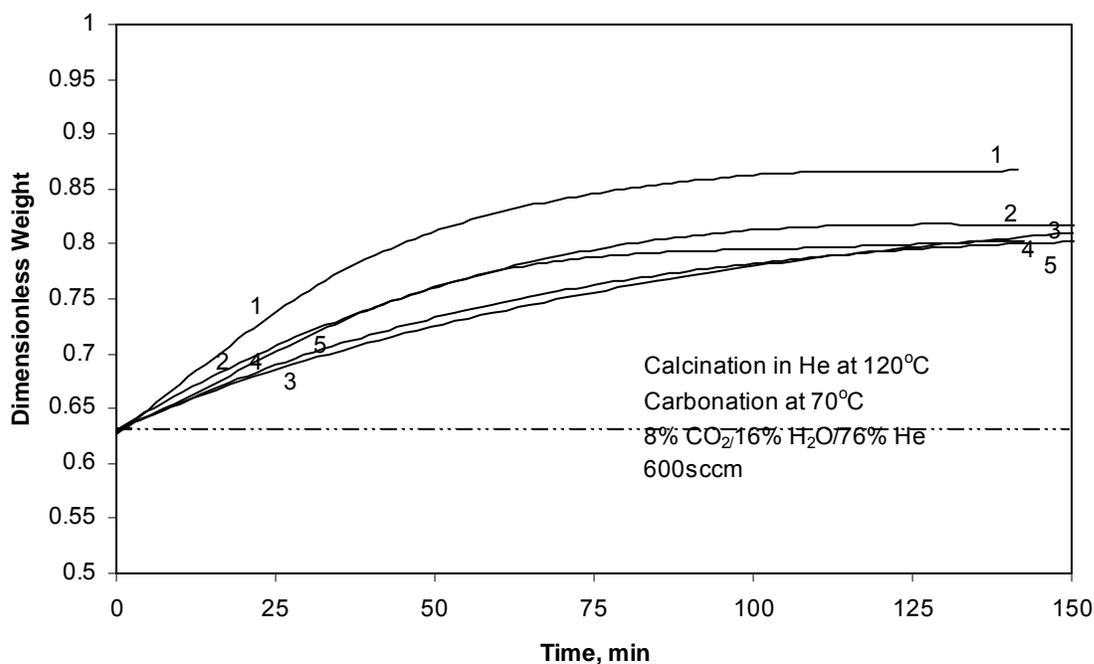


Figure 17. Smoothed electrobalance results for five carbonation cycles using SBC#3: Calcination in He at 120°C

The dimensionless weight of 0.87 after 150 min in carbonation Cycle 1, which corresponds to 108% conversion to Wegscheider’s salt, is in reasonable agreement with previous single-cycle results. The 150-min dimensionless weights then decreased to 0.82, 0.81, 0.80, and 0.80, in Cycles 2 through 5, respectively, with the final value of 0.80 corresponding to about 76% conversion of Na_2CO_3 to Wegscheider’s salt.

Similar raw electrobalance data from a five-cycle run using SBC#3, but with calcination at 200°C in CO_2 , are shown in Figure 18. Once again, complete calcination was obtained in each cycle. The final dimensionless weight at the end of the first carbonation cycle was 0.83, which corresponds to about 90% conversion to Wegscheider’s salt. There were small decreases in the initial slope with increasing cycle number, but the magnitudes of the decreases were smaller than shown in Figure 16. Similarly, there was a small decrease in final dimensionless weight between Cycles 1 and 2, but no further decrease between Cycles 2 and 5.

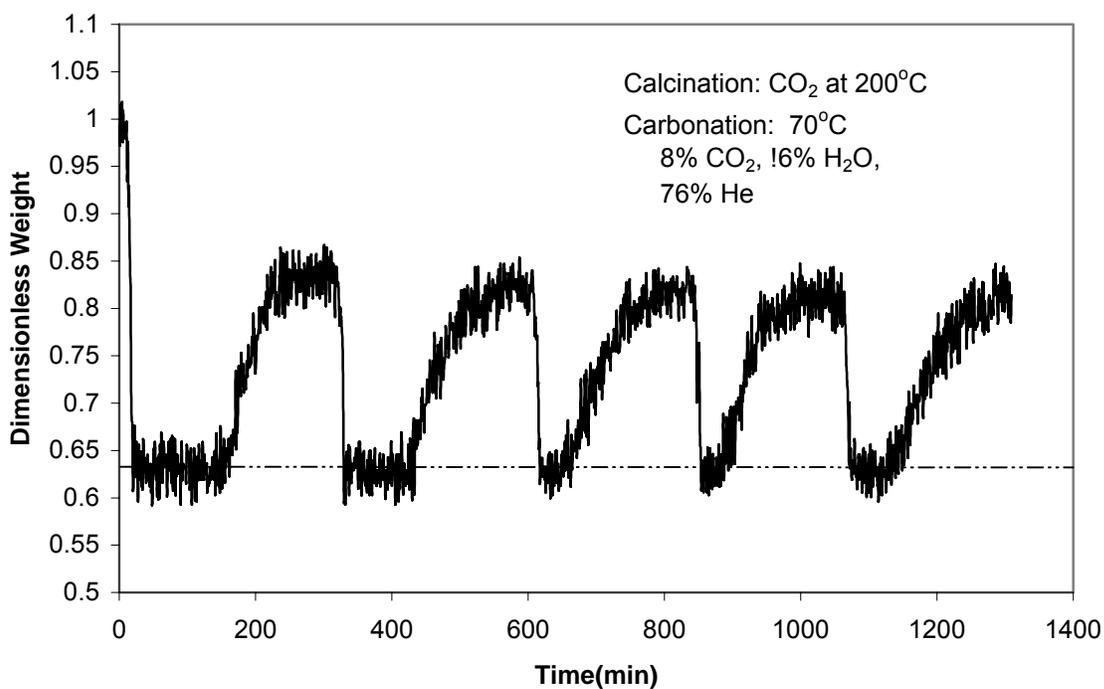


Figure 18. Raw electrobalance results for five-cycle test using SBC#3: Calcination in CO₂ at 200°C

Smoothed dimensionless weight-time data from a five-cycle test using trona T-200 are shown in Figure 19. Calcination conditions were 120°C in He, the same as used in the five-cycle test with SBC#3 whose results are shown in Figure 17. Note that the reproducibility problems associated with trona samples did not exist in this case because the same sample was used in each cycle. The final dimensionless weights in all cycles were about 0.92, which corresponds to about 87% carbonation. Sorbent durability appears to be superior to that of SBC#3, as there are no significant decreases in either the initial slopes of the curves or the final dimensionless weights.

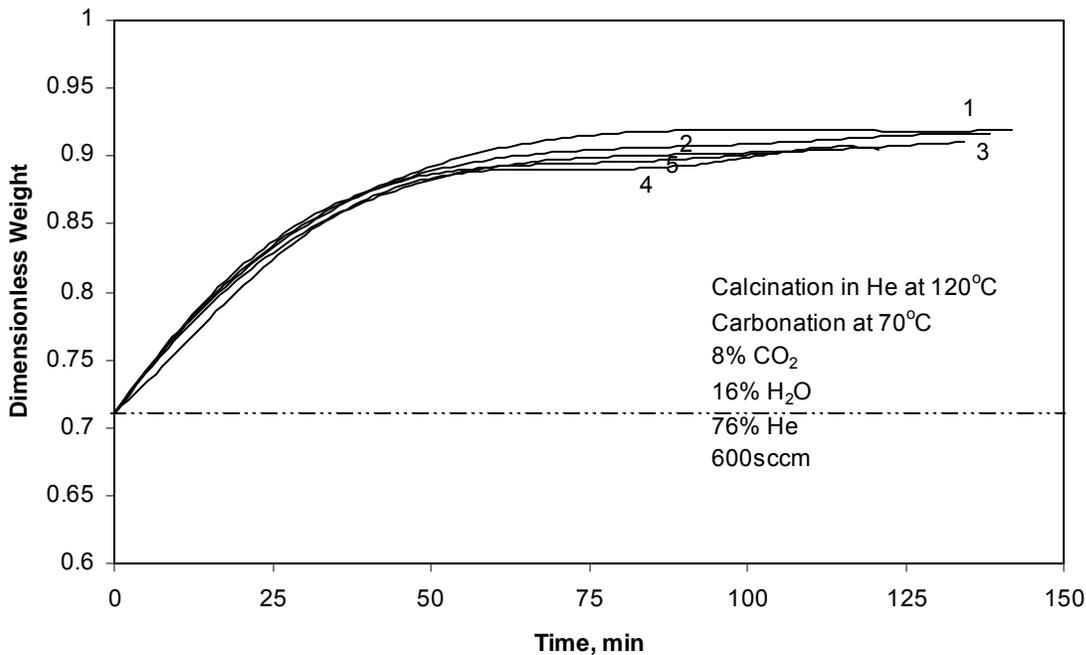


Figure 19. Smoothed electrobalance results for five carbonation cycles using Trona T-200: calcination in He at 120°C

3.1.3 Fractional Carbonation Versus Cycle Number Results

In this section, fractional carbonation values at selected reaction times are used instead of the complete dimensionless weight versus time curves presented in the previous section. This facilitates comparison of results from different runs. Fractional conversion as a function of time is given by equations 7 through 12. Also in this section, $t = 25 \text{ min}$ was chosen to represent the reaction rate and $t = 150 \text{ min}$ was chosen to approximate the final fractional carbonation.

The reproducibility of three five-cycle tests using different samples of SBC#3 is shown in Figure 20. Calcination was carried out at 120°C in He and the results from the five-cycle test previously presented in Figure 17 are included. The discrete points represent individual test results while the line is drawn through the average from the three tests. The scatter between runs is obvious, particularly in the $f(25)$ data. While there is a general decrease in $f(25)$ with cycle number, there is no consistent trend. The largest single value of $f(25)$ occurred in Cycle 4 of one of the tests, and, probably by coincidence, the $f(25)$ values in Cycle 4 were larger than the Cycle 3 values in each test. There is less scatter in the $f(150)$ results, as well as a clear decrease from Cycles 1 to 2 to 3, followed by reasonably constant values in Cycles 3, 4, and 5.

The average values of $f(25)$ and $f(150)$ in Cycle 5 are 29% and 23%, respectively, smaller than the corresponding values in Cycle 1.

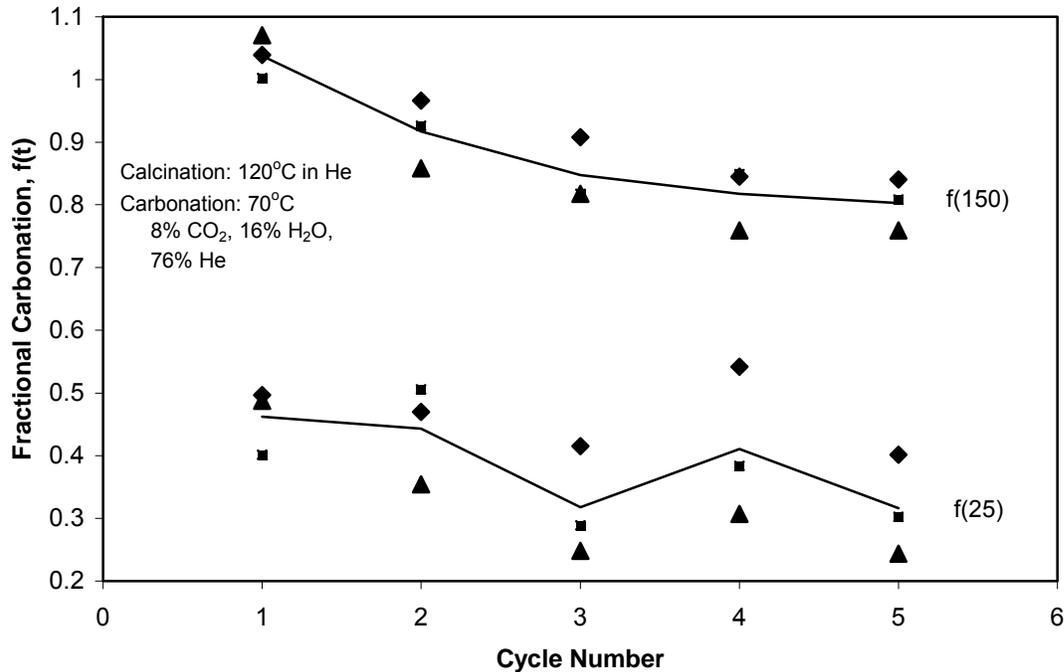


Figure 20. $f(25)$ and $f(150)$ from three duplicate tests using SBC#3: Calcination at 120°C in He

Similar results were obtained from three duplicate five-cycle tests at the same conditions using trona T-200. The average value of $f(150)$ decreased by 12%, from 0.90 in Cycle 1 to 0.79 in Cycle 5, while the average value of $f(25)$ decreased by 27%, from 0.51 in cycle 1 to 0.37 in Cycle 5.

The effects of calcination temperature and atmosphere on reaction rate, $f(25)$, and capacity, $f(150)$, in five-cycle tests using SBC#3 are shown in Figures 21 and 22, respectively. All carbonations occurred at 70°C in 8% CO₂, 16% H₂O, and 76% He. The average values from Figure 20 are used to represent results at 120°C in He, where duplicate tests were made. Calcination at 200°C in an atmosphere of 20% H₂O and 80% CO₂ was added in this series of tests to simulate possible commercial calcination conditions.

The maximum carbonation reaction rate, represented in Figure 21 by $f(25)$, clearly occurred following calcination at the mildest conditions of 120°C in He. Results at the more severe calcination conditions were closely bunched, except for unexpectedly high results in Cycles 2

and 4 for calcination at 200°C in 80% CO₂ and 20% H₂O. Average slopes of all lines in Figure 21 are approximately equal, suggesting that the rate of decrease in activity was not a strong function of calcination conditions. Sorbent capacity data, shown in Figure 22 and represented by $f(150)$, contained less scatter. In particular, in Cycle 1 all values of $f(150)$ were reasonably close to 1.0. Values of $f(150)$ decreased moderately with increased number of cycles at all calcination conditions, with the only exception being Cycles 4 and 5 following calcination in He at 160°C.

The $f(25)$ and $f(150)$ carbonation results for four test sorbents—SBC#1, SBC#3, T-50, and T-200—are compared in Figures 23 and 24. Calcination occurred under severe conditions of 200°C in CO₂, while carbonation occurred at 70°C in 8% CO₂, 16% H₂O, and 76% He. SBC#1 produced the largest values of both $f(25)$ and $f(150)$, and there was relatively little decrease in either value with increasing cycle number. For example, the values of $f(25)$ actually increased between Cycles 1 and 4 before decreasing in Cycle 5. The $f(150)$ value decreased by only 10%, from 1.02 in Cycle 1 to 0.92 in Cycle 5. SBC#3 was second to SBC#1 in both $f(25)$ and $f(150)$, and there was relatively little difference in either of the trona samples.

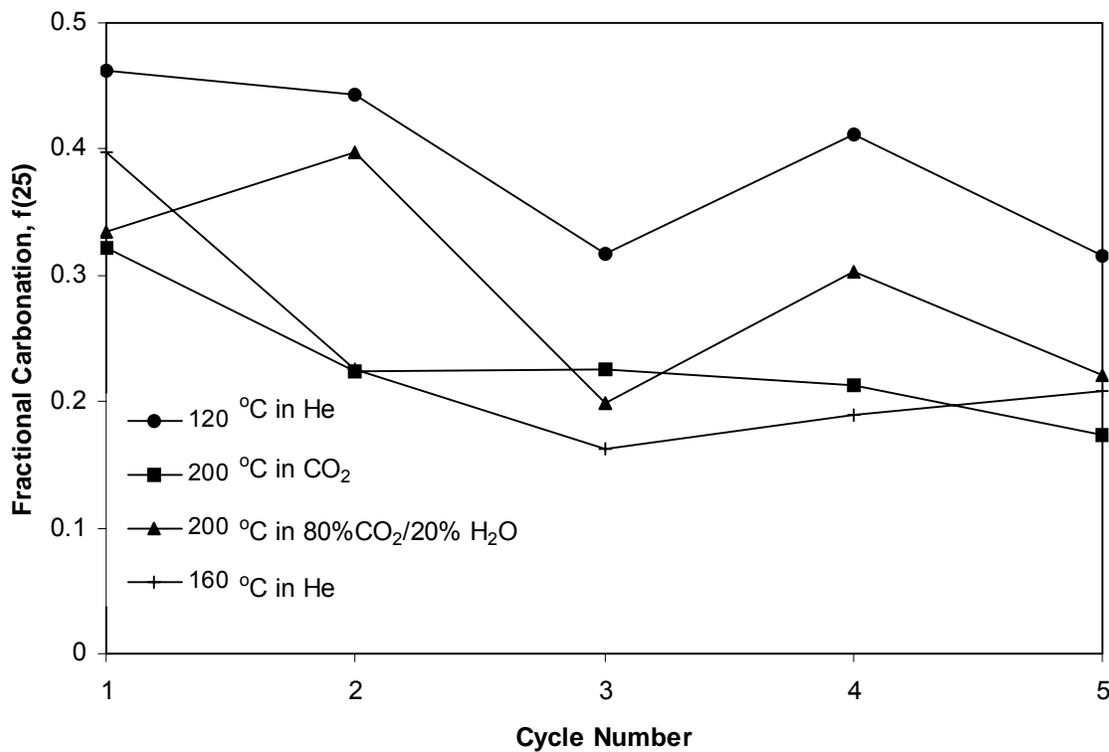


Figure 21. Comparison of $f(25)$ for carbonation of SBC#3 at four calcination conditions

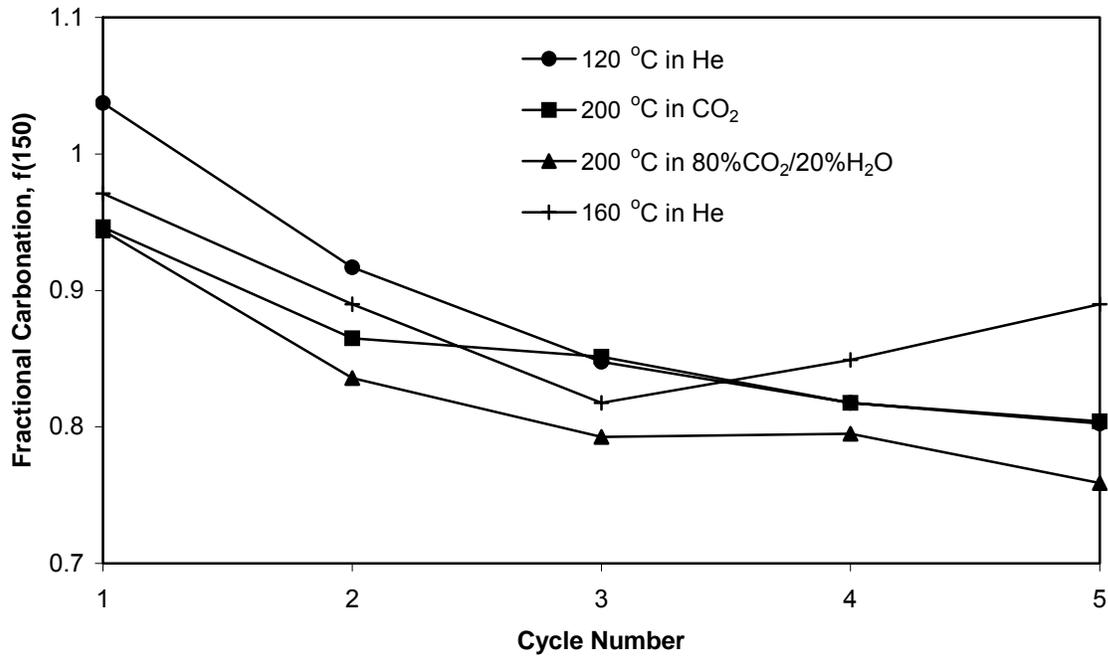


Figure 22. Comparison of $f(150)$ for carbonation of SBC#3 at four calcination conditions

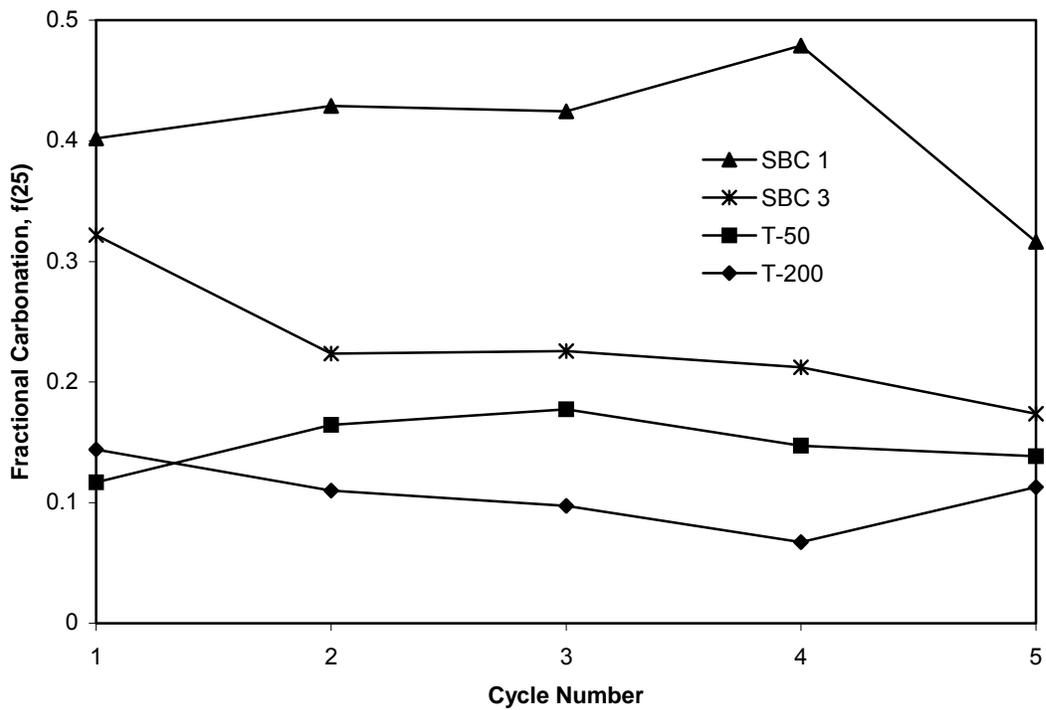


Figure 23. $f(25)$ comparison for four sorbent using 200°C calcination in CO₂

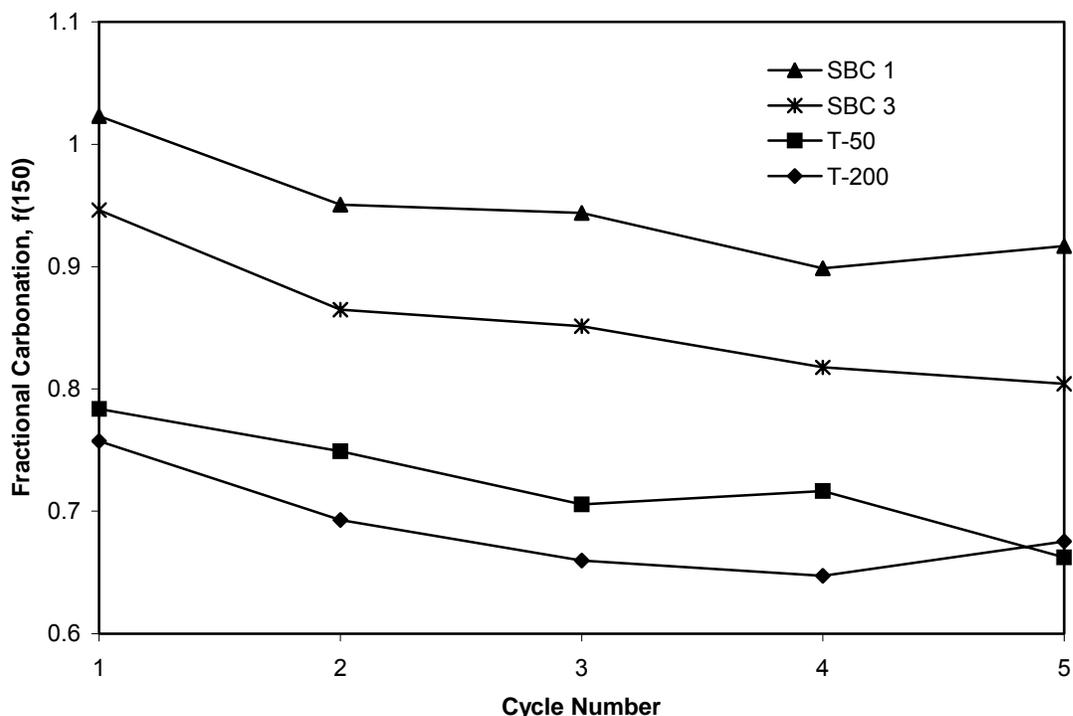
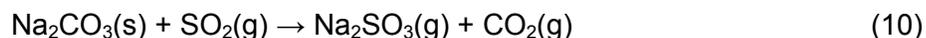


Figure 24. $f(150)$ comparison for four sorbents using 200°C calcination in CO₂

3.1.4 The Effect of SO₂

The presence of SO₂ in the flue gas will interfere with CO₂ removal through the formation of Na₂SO₃ and/or Na₂SO₄. The relevant reactions are



The effect of SO₂ addition, with and without the presence of O₂, was examined in a series of multicycle electrobalance tests. When 0.4% and 0.2% SO₂ were added the tests were terminated after three cycles because little carbonation activity remained. When 0.1% SO₂ was added the test was continued through five cycles with a cumulative loss in CO₂ removal in each cycle. Calcination conditions were 120°C in He in all tests, and carbonation occurred at 70°C in 8% CO₂ and 16% H₂O with the He concentration decreasing in response to the SO₂ that was added.

Figure 25 shows raw electrobalance data for a 3.5-cycle test using SBC#3 in which 0.2% SO₂ was added to the carbonation gas. The initial calcination progressed as expected with the final

dimensionless weight very near the theoretical value of 0.631. The dimensionless weight increased rapidly when the SO₂-containing carbonation gas was added and reached a maximum of about 0.88 about 100 min later. The dimensionless weight then began to decrease and was about 0.83 when the first carbonation cycle ended. The final dimensionless weight at the end of the second calcination was 0.68, instead of 0.63, presumably due to the irreversible formation of Na₂SO₃. The weight changes became progressively smaller thereafter and after the fourth calcination the final dimensionless weight decreased only to 0.74. At the end of the fourth calcination the temperature was increased incrementally to 200°C, but there was no additional weight loss. Not only were increasing amounts of Na₂SO₃ being formed in each carbonation cycle, the Na₂SO₃ was stable in He at temperatures as high as 200°C. The cause of the dimensionless weight maximum, which occurred only during the first cycle, is unknown.

The amount of CO₂ removed during each carbonation cycle is proportional to the difference in dimensionless weights between the end of a carbonation and subsequent calcination cycle. This difference decreased from 0.15 in Cycle 1 (based on the final dimensionless weight of 0.83) to 0.11 in Cycle 2 and to 0.04 in Cycle 3.

Reducing the SO₂ concentration to 0.1% slowed the rate of Na₂SO₃ formation enough that five complete cycles could be completed. Results of a five-cycle test using trona T-200 are shown in Figure 26. The results were qualitatively similar to those shown in Figure 25 except that the rate at which CO₂ sorption capacity was lost decreased because of the lower SO₂ concentration. The dimensionless weight increase was 0.25 during the first carbonation cycle, but was only 0.06 during the fifth carbonation cycle. This represents a loss in CO₂ sorption capacity of about 76% in five cycles.

Results obtained when both 1.7% O₂ and SO₂ were added to the carbonation gas were not greatly different from results shown in Figures 22 and 23. 1.7% O₂ was selected as this approximates the O₂ concentration in flue gas when natural gas is burned with 10% excess air. From these results it is clear that when sulfur-containing fossil fuels are burned, the CO₂ capture step must be downstream of a desulfurization step.

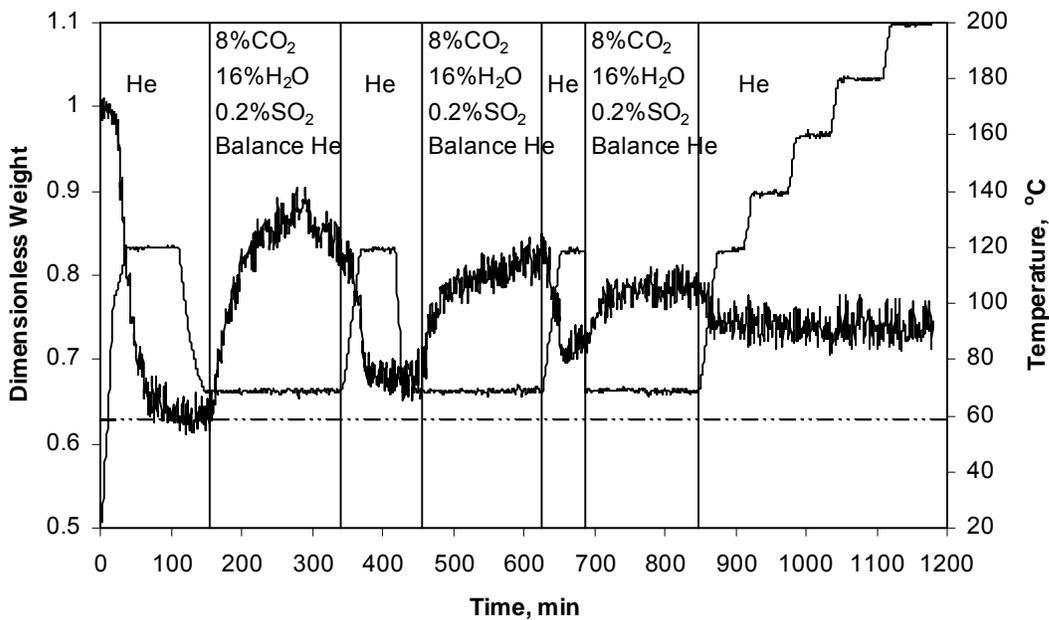


Figure 25. The effect of 0.2% SO₂ added to the carbonation gas: Three cycles using SBC#3

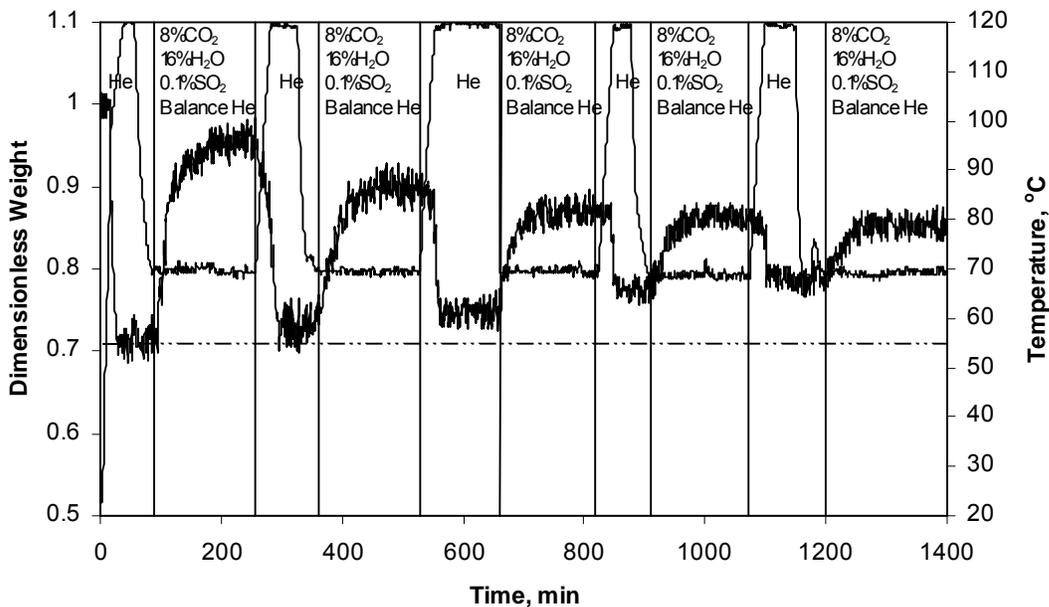


Figure 26. The effect of 0.1% SO₂ added to the carbonation gas: Five cycles using Trona T-200

3.3 FIXED-BED REACTOR TESTING AT LSU

Fixed-bed tests with the product gas analyzed by gas chromatography were used to evaluate CO₂ removal. At the beginning, single cycle tests were carried out to confirm the reliability of the reactor and analytical systems; most of the later tests were multicycle to provide additional information on sorbent durability. Calcination was carried out in both pure N₂ and CO₂ over a temperature range of 120°C to 200°C. The carbonation gas contained 8% CO₂, 16% H₂O, and 76% N₂, and in most tests H₂O was added using a gas bubbler system, the gas exiting the bubbler was assumed to be saturated. Nominal carbonation temperatures of 60°C, 70°C, and 80°C were examined, but the actual bed temperature was somewhat higher because of the exothermic nature of the carbonation reaction. SBC#3 was used as the sorbent in all tests except one, which used SBC#1.

3.3.1 Five-Cycle Tests With Calcination in N₂ at 120°C

CO₂ concentration (dry basis) in the product gas as a function of time during both the calcination and carbonation phases of a 5.5-cycle test using SBC#3 with calcination at 120°C in N₂ and a nominal carbonation temperature of 60°C is shown in Figure 27. As previously described, the initial calcination was carried out one day with both carbonation and calcination on subsequent days. The sorbent was always left overnight as Na₂CO₃ at 60°C in flowing N₂. First-cycle calcination material balance closure was good with only a 3.5% difference between the theoretical amount of CO₂ liberated and the experimental value determined by numerical integration of the CO₂ concentration-time curve. Initial CO₂ concentrations were near 1% in all carbonation cycles except Cycle 1, where the minimum CO₂ concentration was about 3%. There is a clear indication of improved performance between carbonation Cycles 1 and 2, similar to that shown in Figure 5, which illustrated typical results. Results from calcination Cycles 2 through 6 are virtually identical, with a maximum CO₂ concentration of about 15% in each cycle.

These results are indicated more clearly in Figure 28 where CO₂ concentrations in the carbonation product gas during the five cycles are overlaid. The poorer performance during the early stages of Cycle 1 is obvious. With the exception of the waves in the concentration-time curves in the 200–300 min period of Cycles 2 and 5, performance in Cycles 2 through 5 was basically identical. These waves are thought to be caused by variable feed gas composition due to H₂O condensation between the gas bubbler and the reactor. The difficulty in controlling the preheat level to prevent condensation without overheating of the feed gas has been

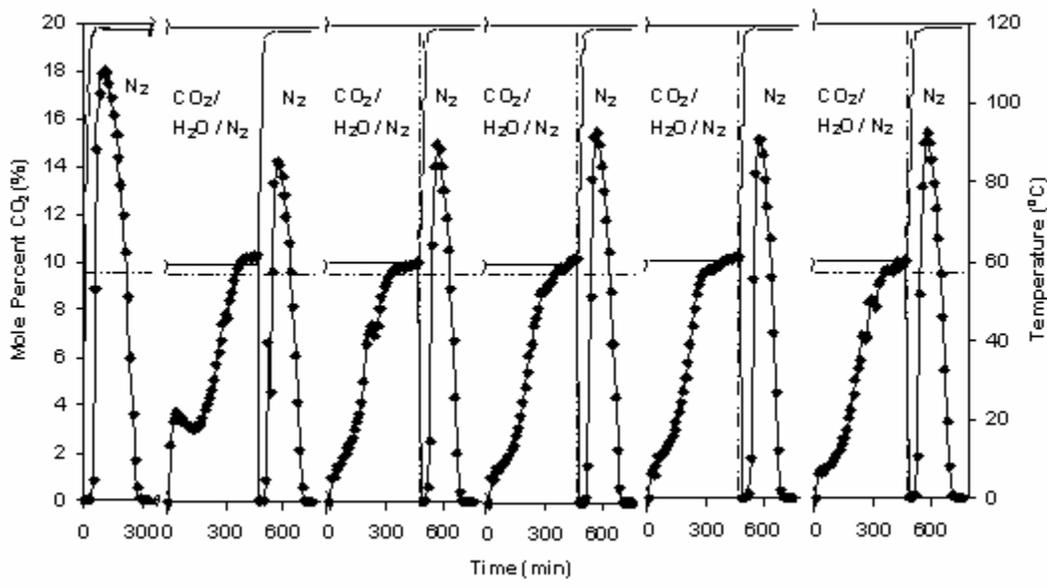


Figure 27. CO₂ concentration for a 5.5-cycle fixed-bed test using SBC#3 at 60°C carbonation temperature and 150 sccm carbonation feed rate

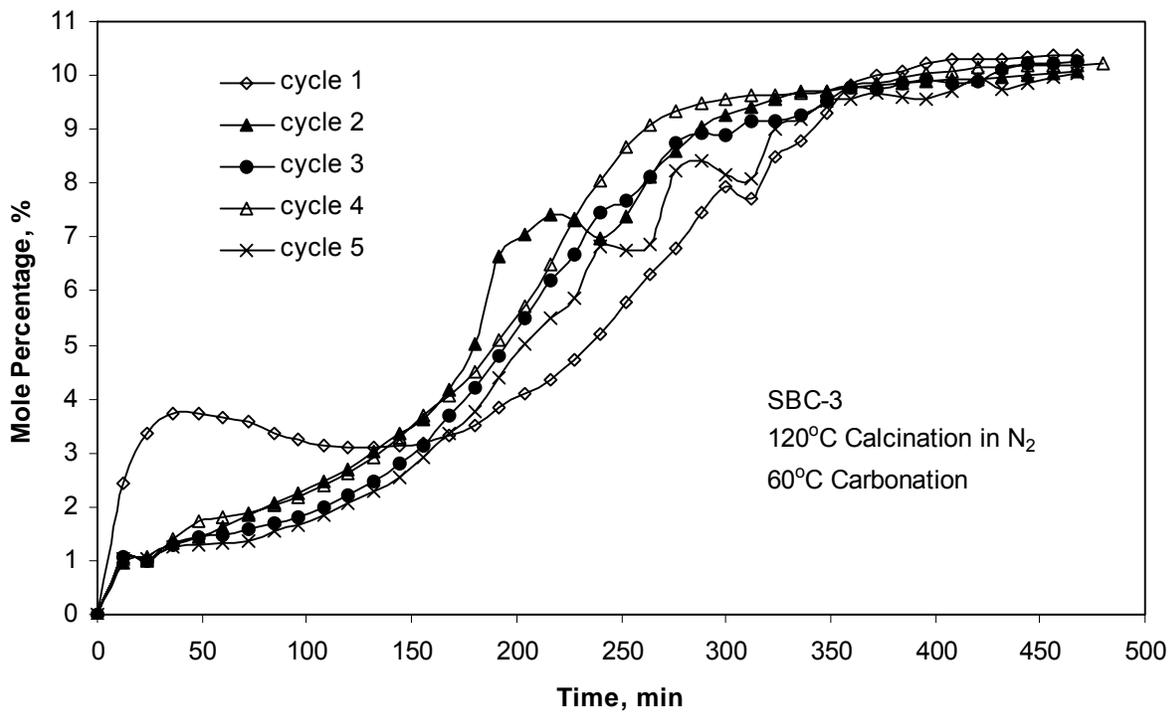


Figure 28. CO₂ concentration during five carbonation cycles using SBC#3 at a nominal carbonation temperature of 60°C and feed rate of 150 sccm

discussed previously. All cycles exhibited the basic shape of a traditional breakthrough curve and all approached almost the same final CO₂ concentration.

Results from the carbonation phases of a five-cycle test using a nominal 70°C carbonation temperature are shown in Figure 29. Calcination was also at 120°C in He in this test. The results are qualitatively similar to the 60°C results shown in Figure 28. There is an obvious improvement in performance between the early stages of Cycles 1 and 2 with effectively no difference in performance between Cycles 2 and 5. The concentration waves are absent and Cycles 2 through 5 all exhibit the shape of a traditional breakthrough curve. The most significant difference between the results at 60°C and 70°C occurred in the early stages of the test. The initial CO₂ concentration at 70°C was about 3% compared to about 1% at 60°C.

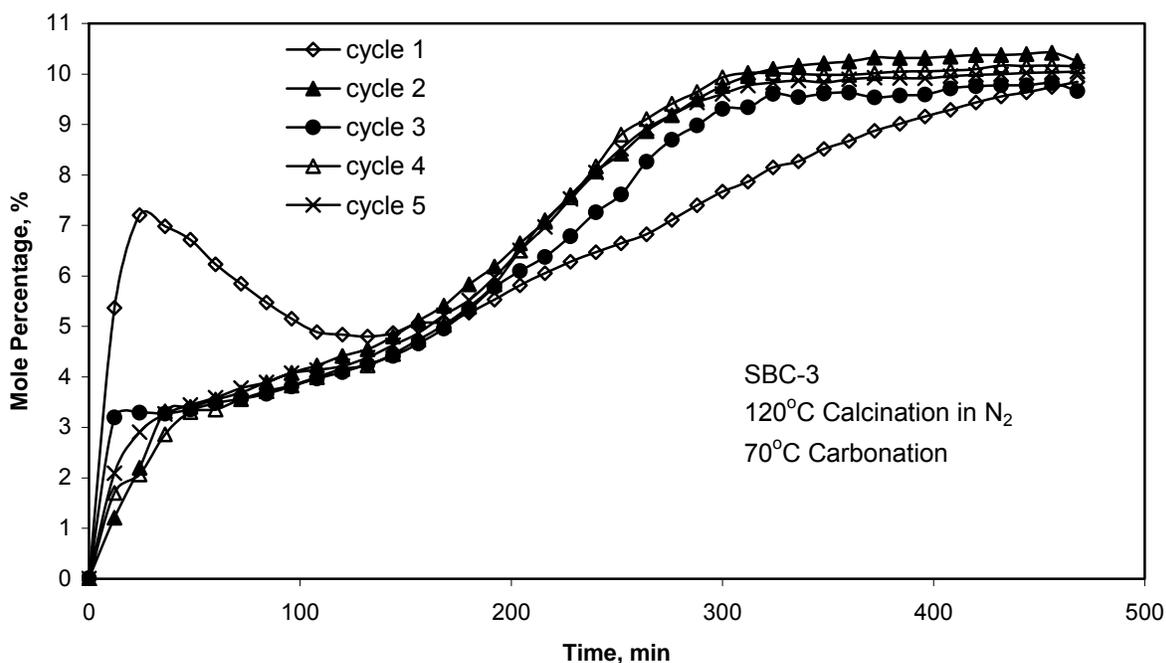


Figure 29. CO₂ concentration during five carbonation cycles using SBC#3 at a nominal carbonation temperature of 70°C and feed rate of 150 sccm

Only a small amount of CO₂ was removed when the carbonation temperature was increased to a nominal 80°C, even though carbonation is thermodynamically favored and some CO₂ removal occurred in electrobalance tests at this temperature. This is attributed to a temperature increase above the nominal level due to the exothermic heat of reaction, and emphasizes the importance of careful temperature control in any commercial process.

SBC#1 was evaluated in a five-cycle test with calcination at 120°C in He and carbonation at a nominal temperature of 60°C. Results from the five carbonation cycles in terms of CO₂ concentration as a function of time are presented in Figure 30. The results are very similar to those shown in Figure 28 for SBC#3 at the same conditions. Again, there was a noticeable improvement in performance between Cycles 1 and 2 and essentially no difference in performance between Cycles 2 and 5. Initial CO₂ concentrations during Cycles 2 through 5 were just over 1%, while the minimum concentration in Cycle 1 was about 2.5%.

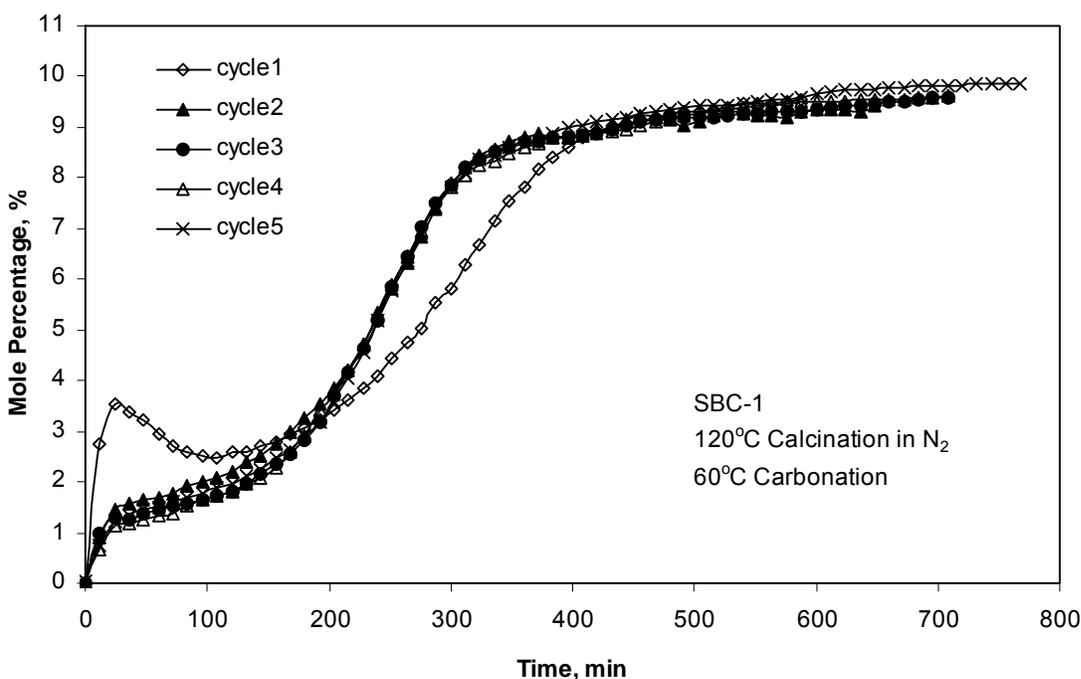


Figure 30. CO₂ concentration during five carbonation cycles using SBC#1 at a nominal carbonation temperature of 60°C and feed rate of 150 sccm.

The performance of SBC#3 and SBC#1 in these five-cycle fixed-bed tests is further compared in Figures 31 and 32. Figure 31 shows the percentage CO₂ removal in the third sample from each carbonation cycle as a function of cycle number. The third sample, which was acquired 36 min after the carbonation reaction was initiated, was chosen for the comparison to provide sufficient time for the carbonation gas feed rate and composition to reach steady-state values. Figure 32 shows the final percentage conversion of Na₂CO₃ to Wegscheider's salt as a function of carbonation cycle.

Figure 31 emphasizes the improved performance in all three tests between Cycles 1 and 2, the improved performance associated with the lower nominal temperature of 60°C, and the close

correspondence in 60°C results between SBC#3 and SBC#1. At 60°C, the CO₂ removal increased from just above 60% in Cycle 1 to almost 90% in the remaining cycles for both sorbents. The comparable numbers for 70°C carbonation were almost 30% CO₂ removal in Cycle 1 and about 70% in the remaining cycles.

The final percentage conversions of Na₂CO₃ to Wegscheider's salt shown in Figure 32 are quite consistent during all five cycles of all three tests. 60°C carbonation resulted in effectively complete conversion, while the percentage conversion of SBC#3 at 70°C was near 85%.

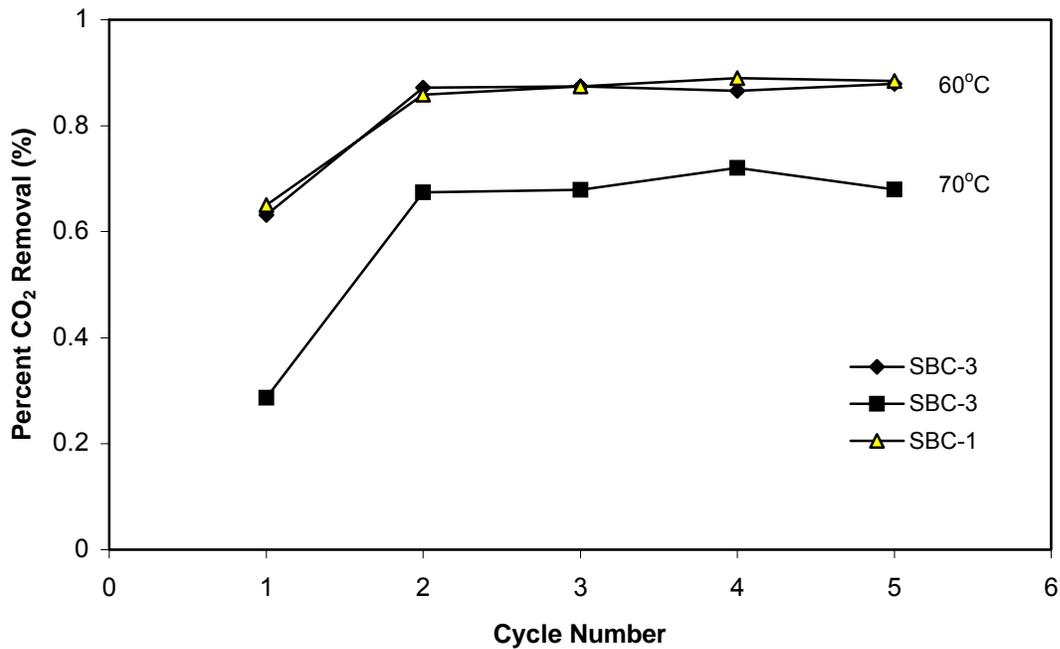


Figure 31. Percentage CO₂ removal as a function of nominal carbonation temperature and cycle number of SBC#3 and SBC#1 (based on CO₂ concentration in the third sample of each carbonation cycle)

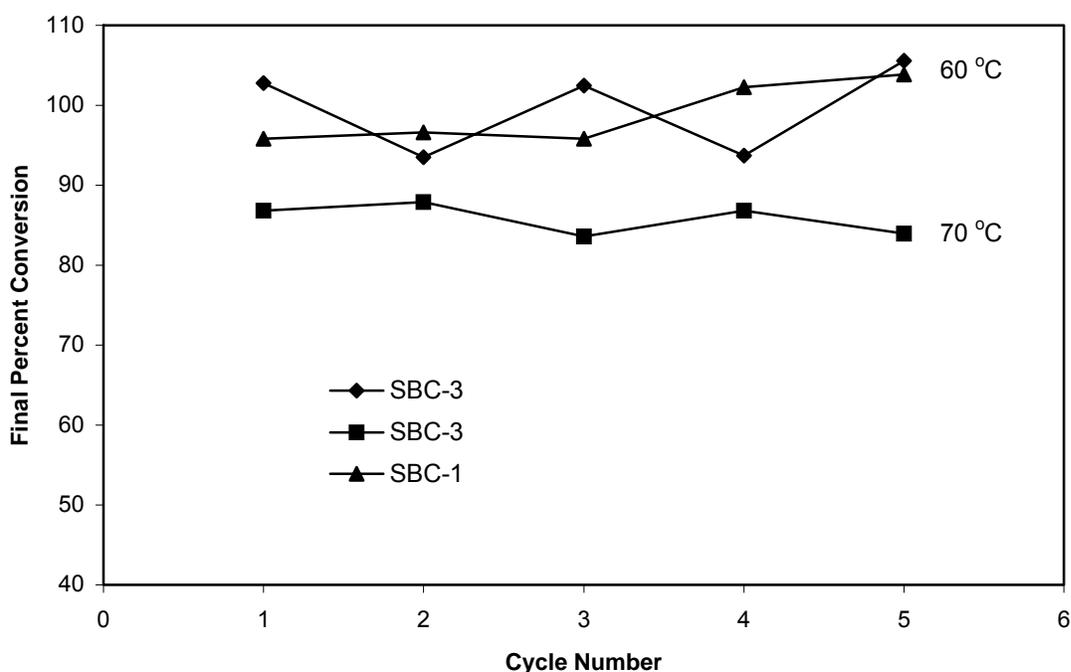


Figure 32. Final percentage conversion of Na₂CO₃ to Wegscheider's salt as a function of carbonation temperature and cycle number using SBC#3 and SBC#1

3.3.2 Multicycle Tests With Calcination in CO₂ at 160°C and 200°C

Carbonation results from two five-cycle tests using SBC#3 with calcination carried out in CO₂ at 160°C are shown in Figures 33 and 34. In these figures, fractional CO₂ removal is shown as a function of time. Progress of the calcination phase cannot be monitored whenever calcination occurs in a CO₂ atmosphere. Consequently, calcination was carried out for a fixed time period of 2 hours. Carbonation was at a nominal temperature of 60°C with the feed containing 8% CO₂, 16% H₂O, and 76% N₂. These figures are, for practical purposes, mirror images of the previous figures, which showed CO₂ concentration as a function of time. The only significant difference in the two tests is that in the first (Figure 33), the carbonation cycle lasted about 350 min; in the second test (Figure 34), the carbonation cycle was ended after 225 min. In earlier tests, the carbonation cycle last as long as 700 min (Figure 30). Figure 33 shows what appears to be a step function increase in CO₂ removal after about 100 min in Cycle 3. This was due, however, to a computer malfunction, which caused the software to incorrectly show 100% CO₂ removal. The carbonation cycle actually continued for the full 350 min in a normal manner. Figure 34 shows two distinct peaks in CO₂ removal during Cycle 1 at about 160 and 190 min. This is attributed to an incorrect level of feed preheat, which allowed partial condensation of H₂O

in the feed gas. The level of preheat was increased slightly in subsequent cycles and the peaks were eliminated.

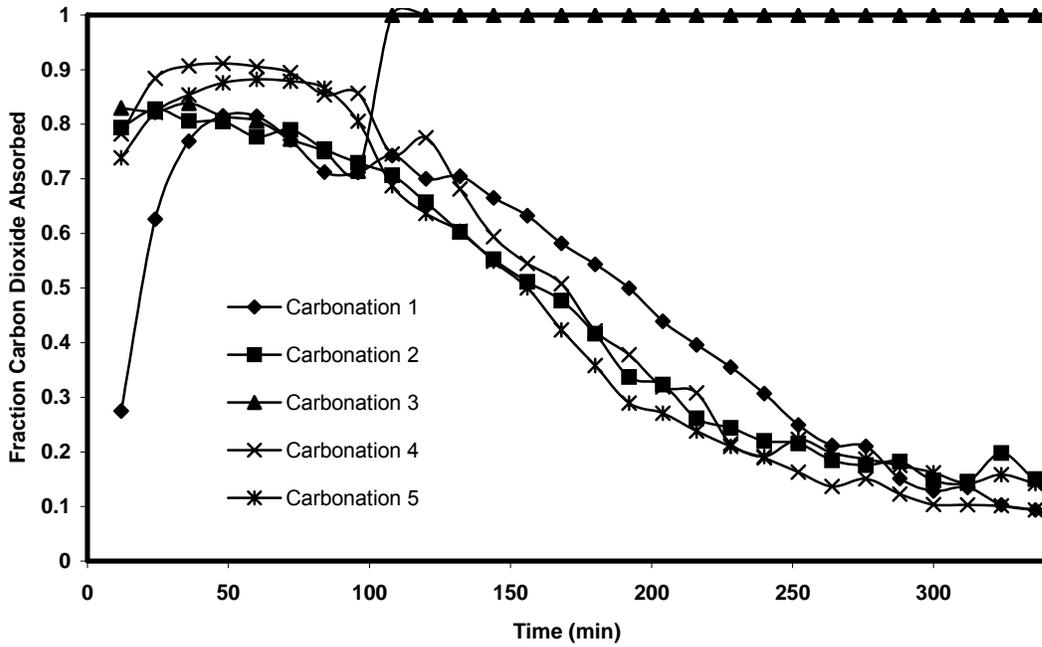


Figure 33. Fractional CO₂ removal as a function of time: Five-cycle testing using SBC#3 with calcination in CO₂ at 160°C, first test

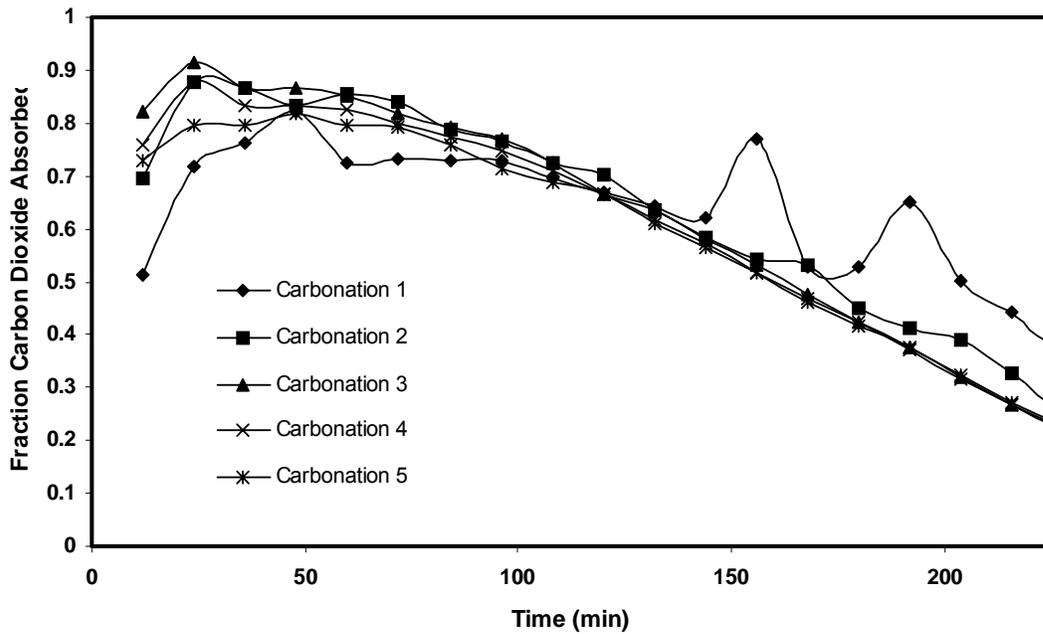


Figure 34. Fractional CO₂ removal as a function of time: Five-cycle test using SBC#3 with calcination at 160°C in CO₂, second test

Both figures show an initial minimum in first-cycle CO₂ removal, followed by an increase to a maximum value and then a gradual decrease with time. In the first cycle of the first test (Figure 33) the CO₂ removal increased from less than 0.30 in the first sample to a maximum of 0.82 after 48 min and slowly decreased to 0.09 at the end of the cycle. The first cycle minimum was less pronounced in the second test (Figure 34) where the CO₂ removal increased from 0.51 in the first sample to a maximum of 0.82 after 48 min and a final value of 0.40 after 225 min. However, the final value may be abnormally high because of the earlier peaks in apparent CO₂ removal.

Performance improved between Cycles 1 and 2 in both tests and remained relatively constant during Cycles 2 through 5. The initial minima were absent, or at least much less pronounced, in subsequent cycles and the overall maxima in CO₂ removal reached 0.91 in both tests. This occurred after 48 min in Cycle 4 in the first test (Figure 33) and after 24 min in Cycle 3 in the second test (Figure 34). Final CO₂ removals ranged from 0.09 to 0.14 when the carbonation cycles were terminated after 350 min in the first test, and from 0.18 to 0.25 when the carbonation cycles were terminated after 225 min in the second test (neglecting the final value of 0.40 in Cycle 1 which is attributed to the condensation problem). Overall, there was little difference between cycles in either test and no evidence of performance deterioration as the number of cycles increased.

Fractional CO₂ removal as a function of time for a five-cycle test using SBC#3 with calcination in CO₂ at 200°C for 2 hours is shown in Figure 35. Once again, the carbonation cycle was at a nominal temperature of 60°C with the feed gas containing 8% CO₂, 16% H₂O, and 76% N₂; the carbonation cycles were again terminated after 225 min.

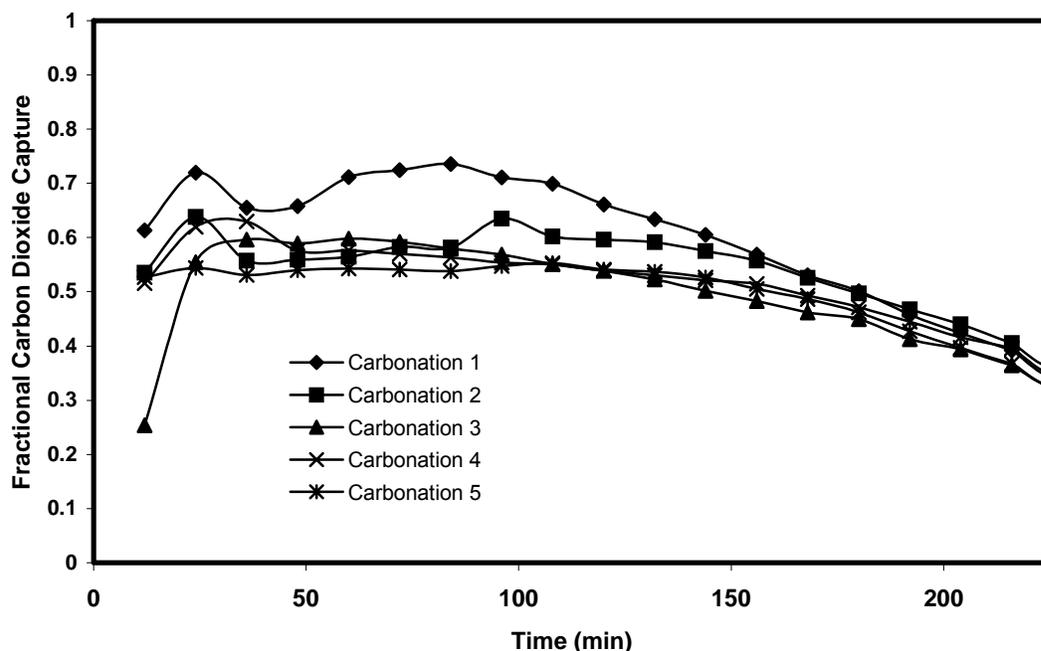


Figure 35. Fractional CO₂ removal as a function of time: Five-cycle test using SBC#3 with calcination in CO₂ at 200°C

While the fractional CO₂ removal-time curves in the last three figures are qualitatively similar, there are significant differences. Once again, the initial minima in CO₂ removal during the first cycle are evident, and the minima are significantly reduced in subsequent cycles. However, performance was significantly poorer using 200°C calcination in CO₂. The overall maximum CO₂ removal was only 0.74 (after 84 min in Cycle 1) compared to 0.91 in both tests following calcination in CO₂ at 160°C. The slopes of the curves in Figure 35 are significantly smaller than the slopes in the previous figures, indicating that CO₂ removal was still occurring to a greater extent when carbonation was terminated. In fact, final CO₂ removals ranged from 0.34 to 0.38 in Figure 35, values that are 50% to 100% larger than in the earlier figures.

Results from these three tests plus a final 15-cycle test are further compared in Figure 36, where fractional CO₂ removal in the third sample of each carbonation cycle is plotted against cycle number. The 15-cycle test used calcination at 160°C in CO₂. As described previously, the third sample was chosen for the comparison to provide sufficient time for feed gas composition and flow rate to reach steady values. The similarity of the results of the three tests using 160°C calcination and the superiority of these tests compared to the 200°C calcination test is immediately evident. There appears to be no deterioration in performance as the number of

cycles increased. It is also interesting to note that fractional CO₂ removals of about 0.90 associated with 160°C calcination in CO₂ are quite close to the values shown in Figure 31 for calcination at 120°C in N₂.

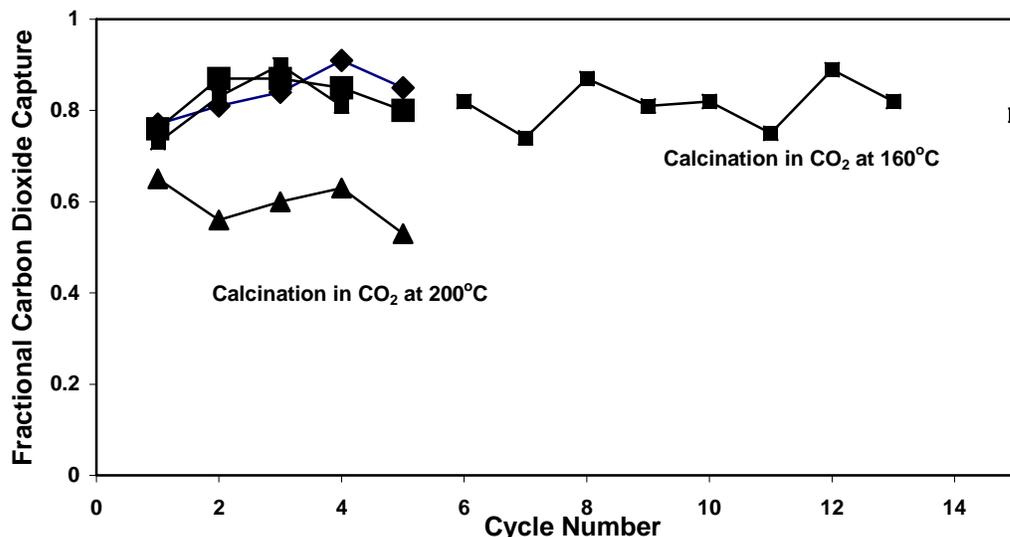


Figure 36. Fractional CO₂ Removal in the third carbonation sample as a function of cycle number: SBC#3 with calcination in CO₂ at 160°C and 200°C

3.4 FLUIDIZED-BED REACTOR TESTING AT RTI

3.4.1 Test 1: SBC#3

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

the carbon dioxide content of the reactor effluent gas and, in all cases, monitored bed temperatures.

Carbon dioxide removal was calculated based on inlet flows (dry basis) of air, nitrogen, and CO₂, and CO₂ content (dry basis) of the effluent gas. Carbon dioxide removal profiles for each cycle are shown in Figures 37 through 41. Cycle lengths varied from approximately 3 to 6.5 hours. Temperature profiles at 1 in, 3 in, and 5 in above the flow distributor are shown in Figures 42 through 46.

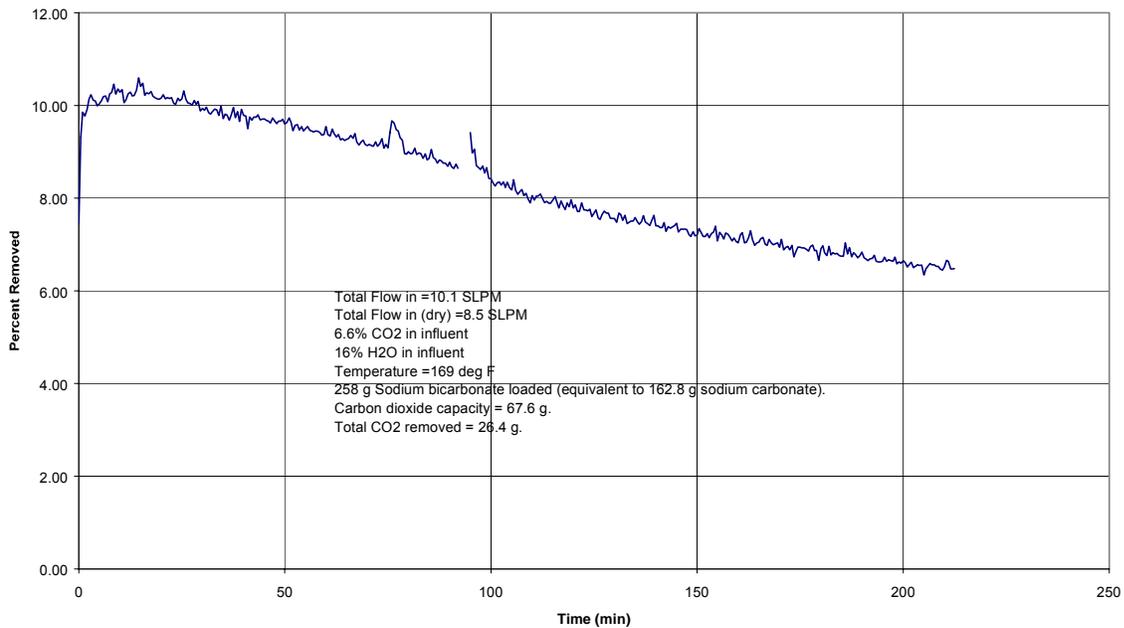


Figure 37. Cycle 1 carbonation test (9/19/01) - fractional CO₂ removal

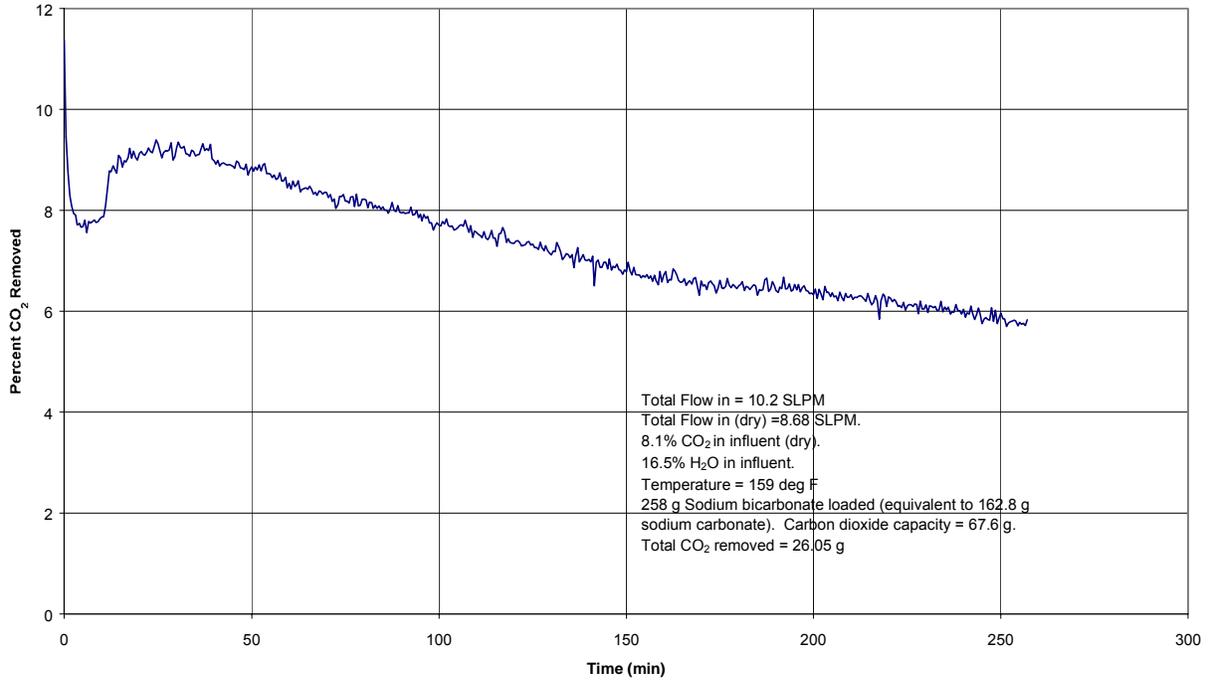


Figure 38. Cycle 2 carbonation test (9/20/01) - fractional CO₂ removal

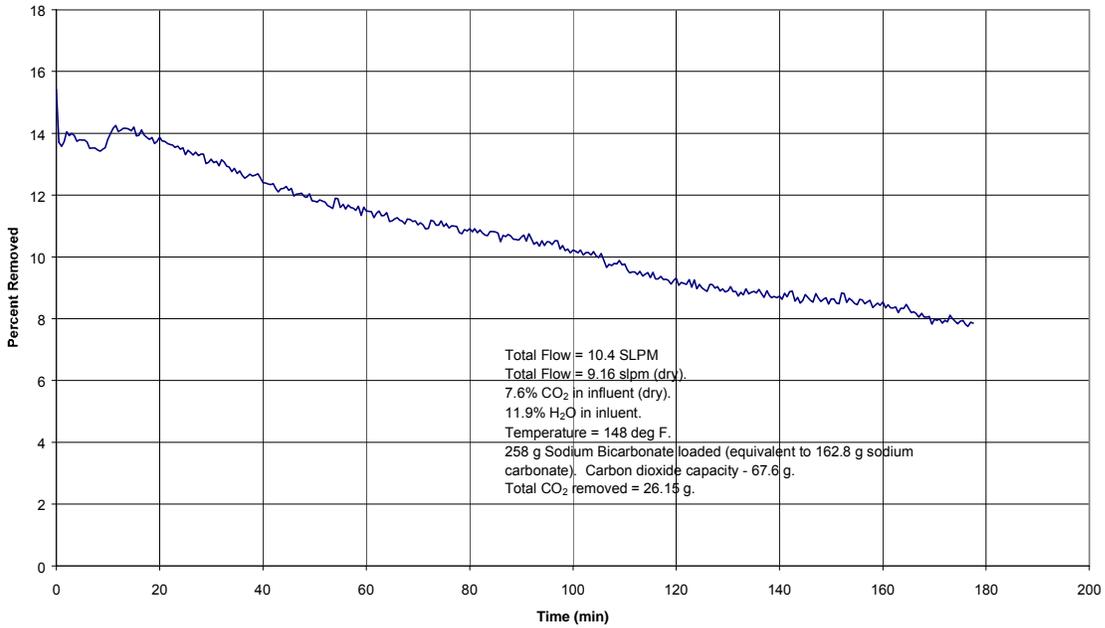


Figure 39. Cycle 3 carbonation test (9/25/01) - fractional CO₂ removal

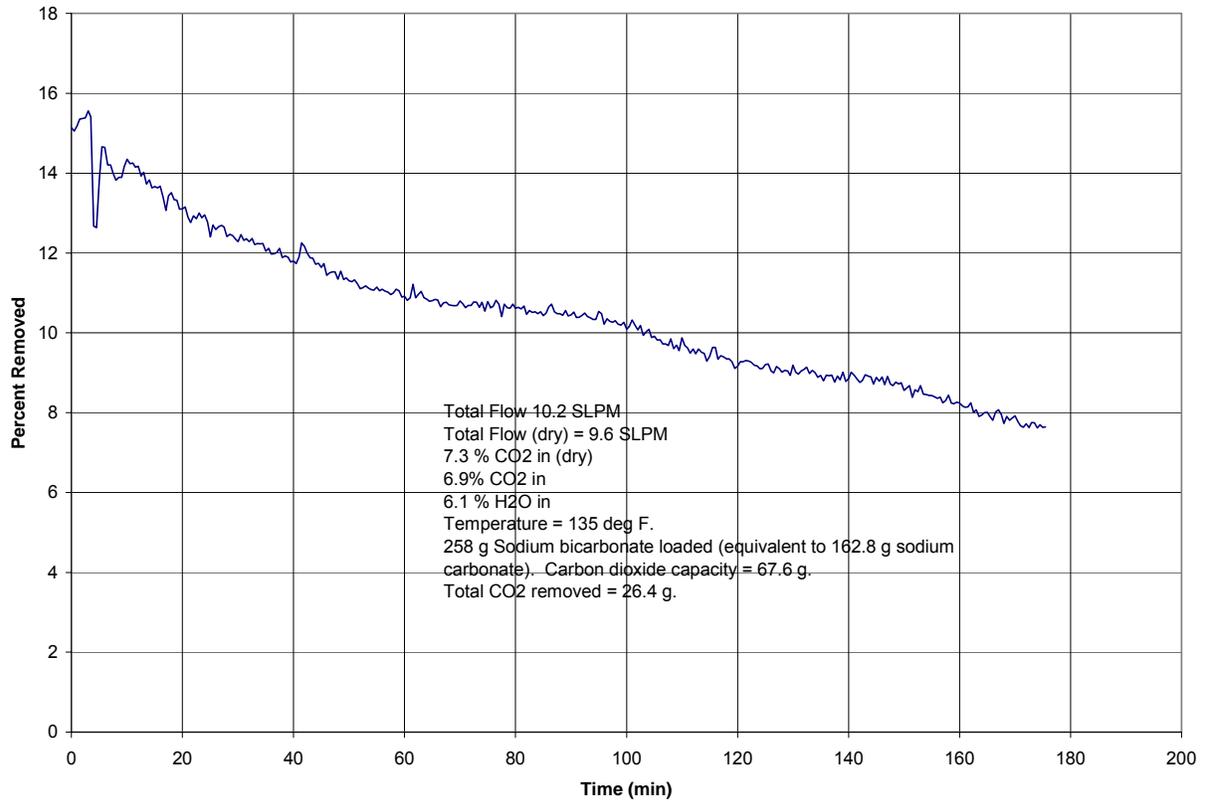


Figure 40. Cycle 4 carbonation test (9/26/01) - fractional CO₂ removal

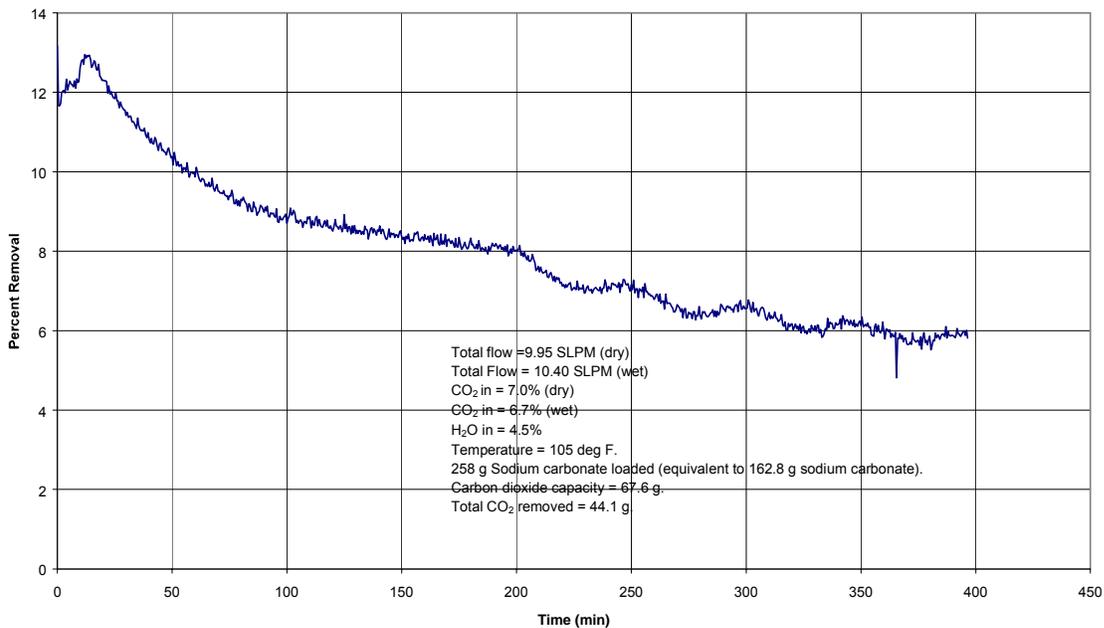


Figure 41. Cycle 5 carbonation test (9/27/01) - fractional CO₂ removal

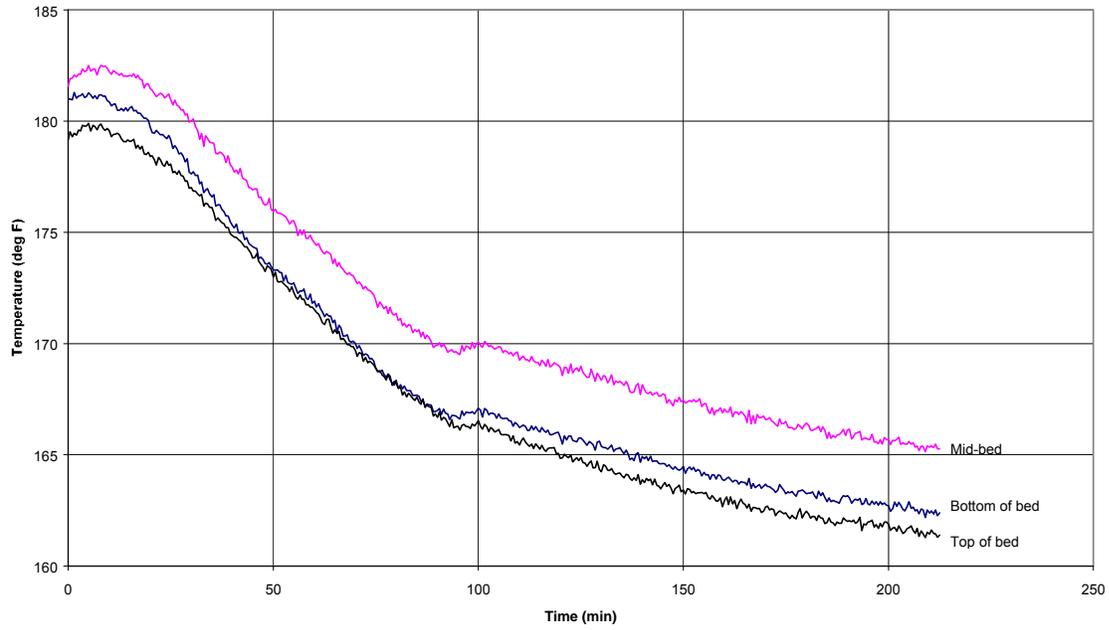


Figure 42. Temperature profile - Cycle 1 (9/19/01)

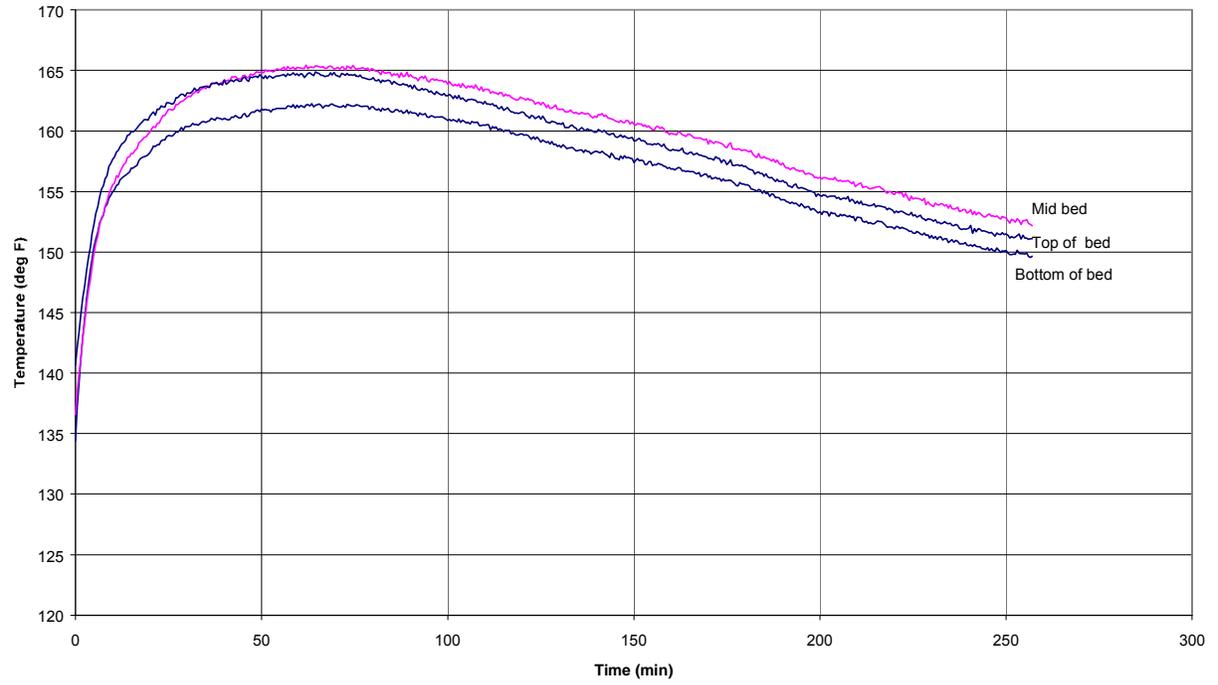


Figure 43. Temperature profile - Cycle 2 (9/20/01)

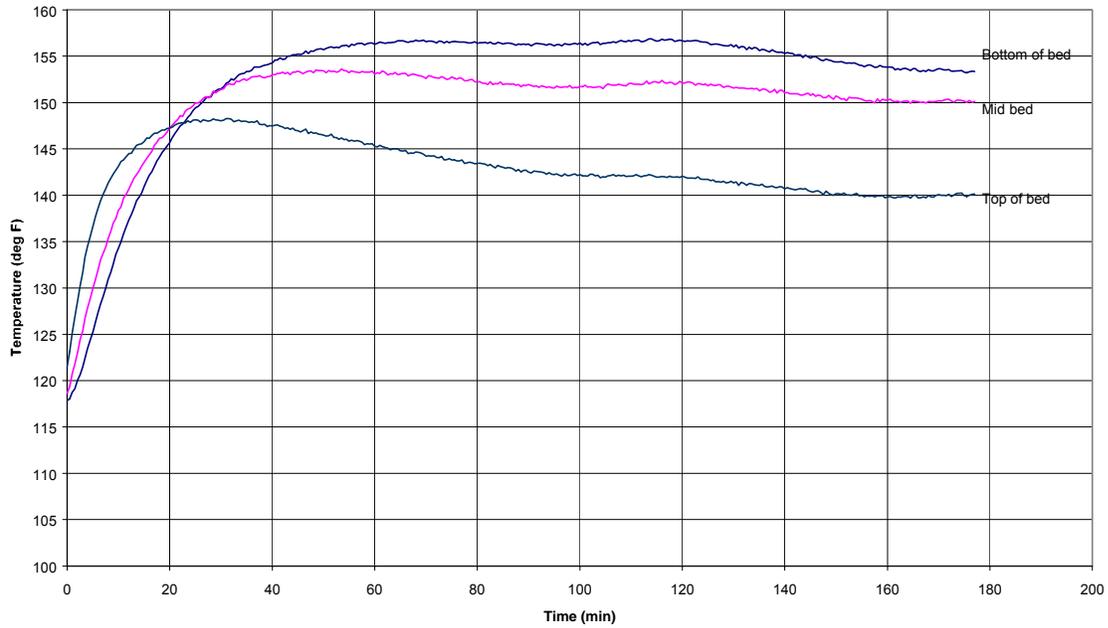


Figure 44. Temperature profile - Cycle 3 (9/25/01)

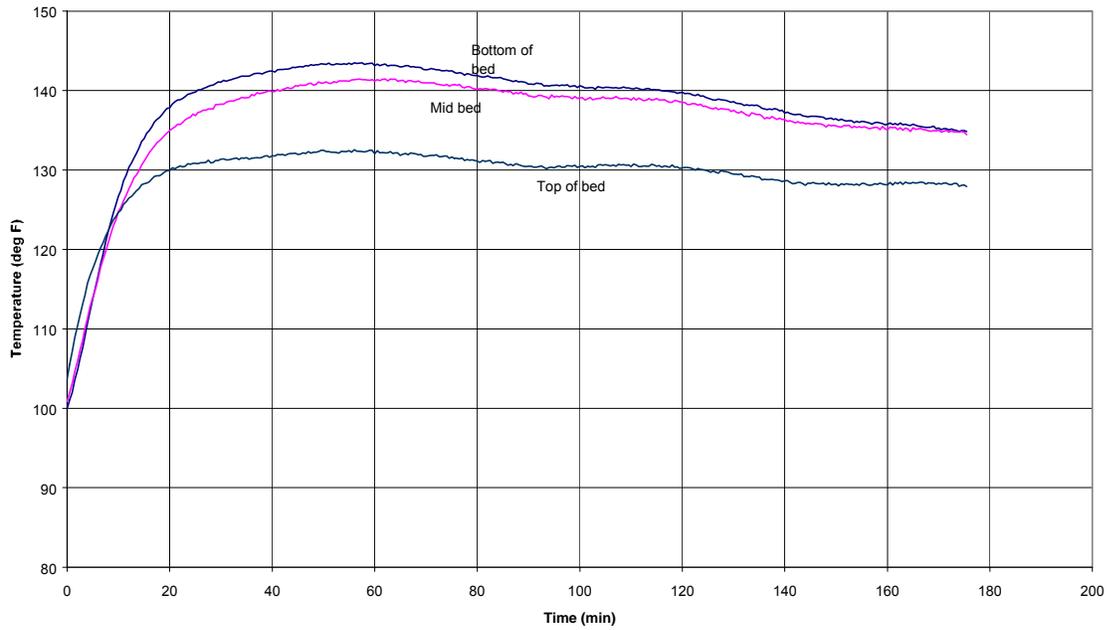


Figure 45. Temperature profile - Cycle 4 (9/26/01)

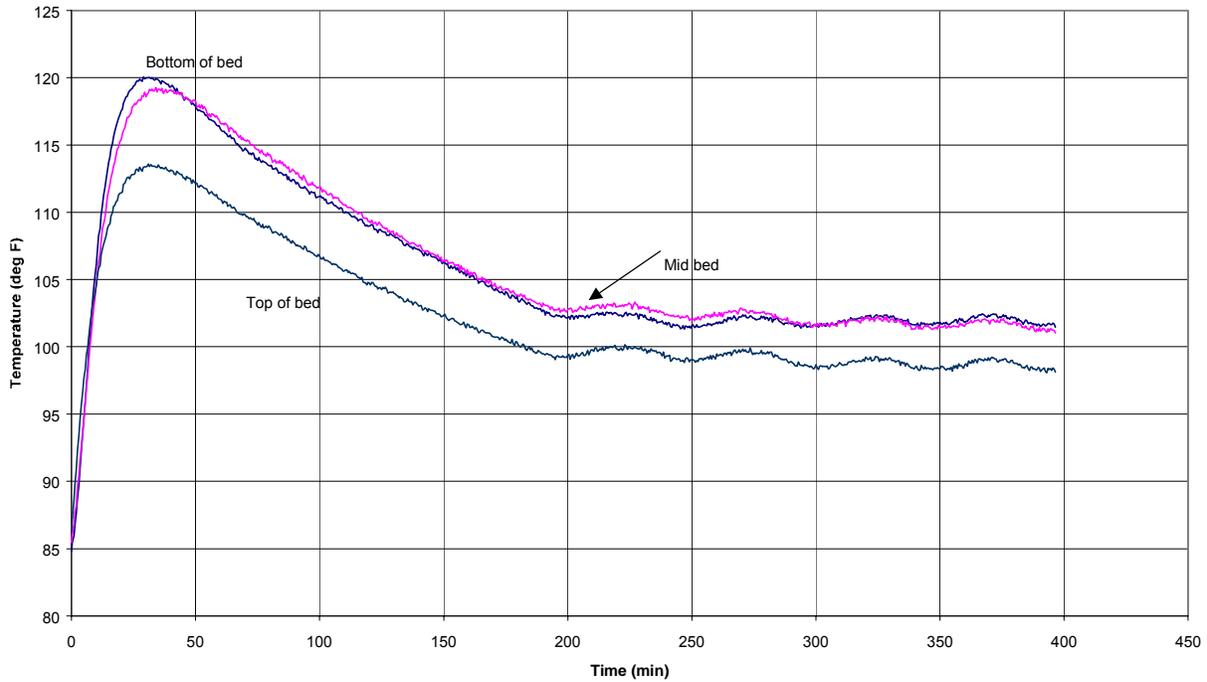


Figure 46. Temperature profile - Cycle 5 (9/27/01)

A summary of test results is given in Table 1. 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.

Table 1. Summary of Five-Cycle Carbonation Test Data

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

Based on these data there was no obvious decline in sorbent activity over five cycles in contaminant-free simulated flue gas. The sorbent was removed from the reactor after the fifth cycle.

3.4.2 Test 2: Trona T-50

This cyclic calcination/carbonation test was limited to two cycles due to plugging of the reactant in the bed. 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 47, 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 determined by comparison of the inlet and outlet carbon dioxide mass flow), as shown in Figure 48, 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 (or 34.3 g based on a Wegscheider's salt endpoint). The sorbent was then calcined in the reactor in the same manner that it was calcined before the first carbonation cycle.

The second carbonation cycle was conducted at a lower, theoretically more favorable temperature, averaging 65°C. Bed temperature profiles are shown in Figure 49. 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 50, declined from 11% to 1% over the course of 160 minutes.

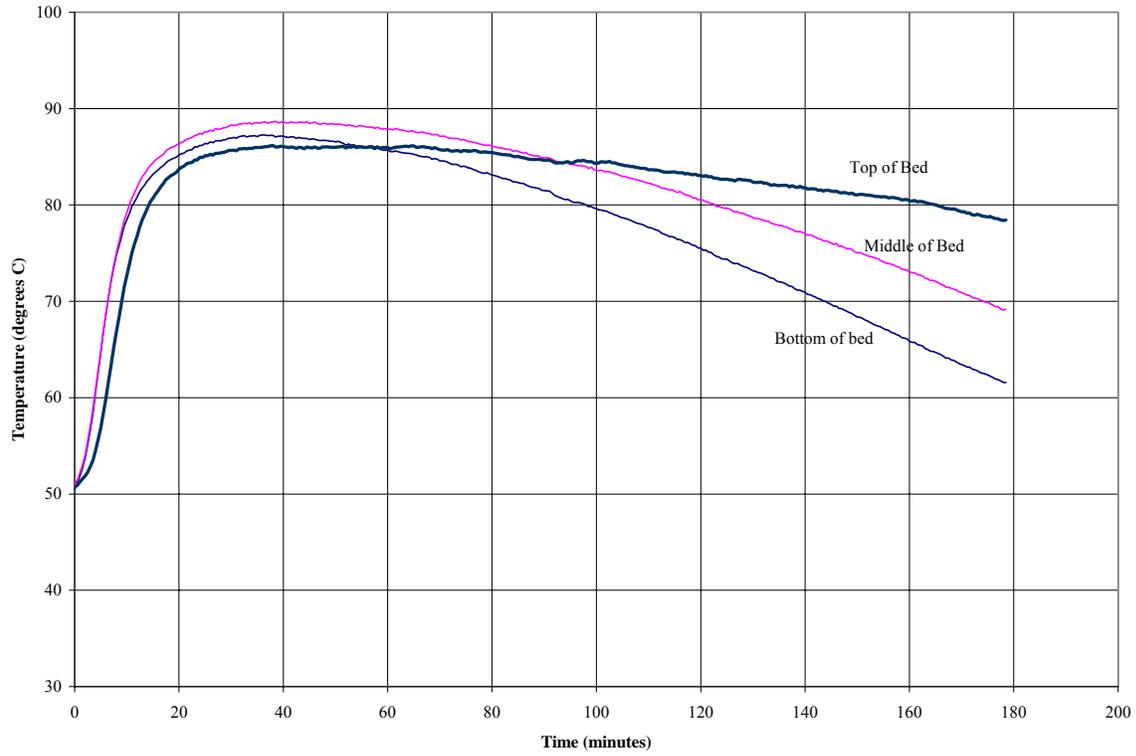


Figure 47. Temperature profile - Cycle 1 with Trona T-50

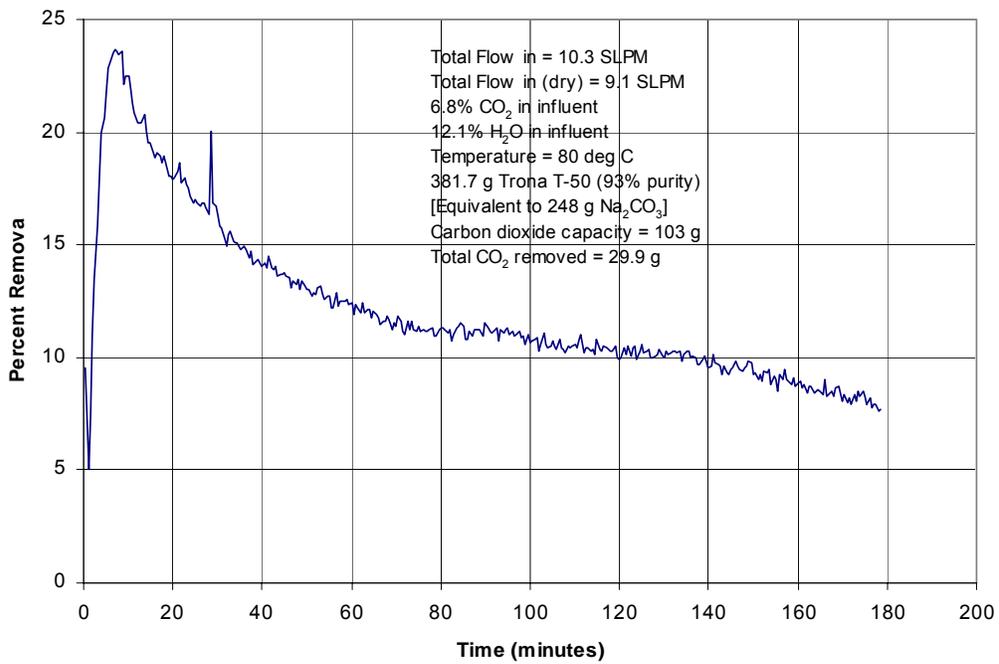


Figure 48. Cycle 1 carbonation test with Trona T-50

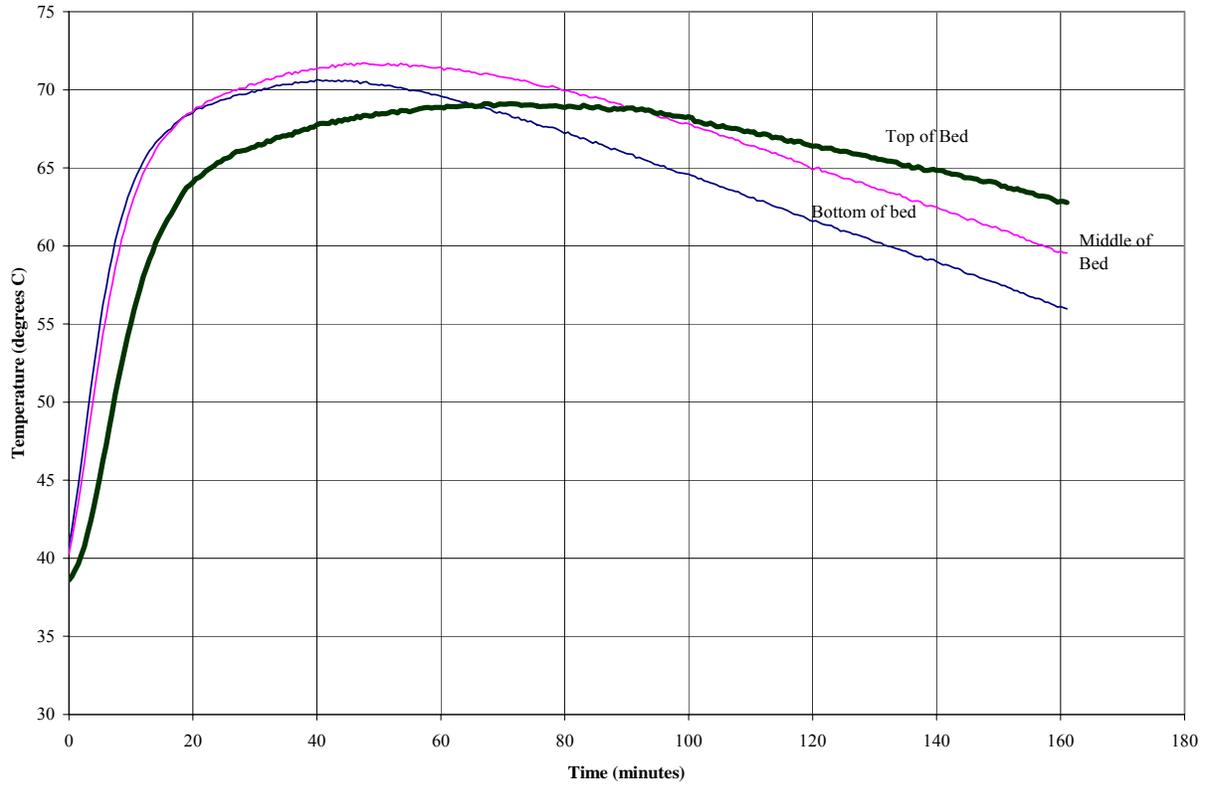


Figure 49. Temperature profile - Cycle 2 with Trona T-50

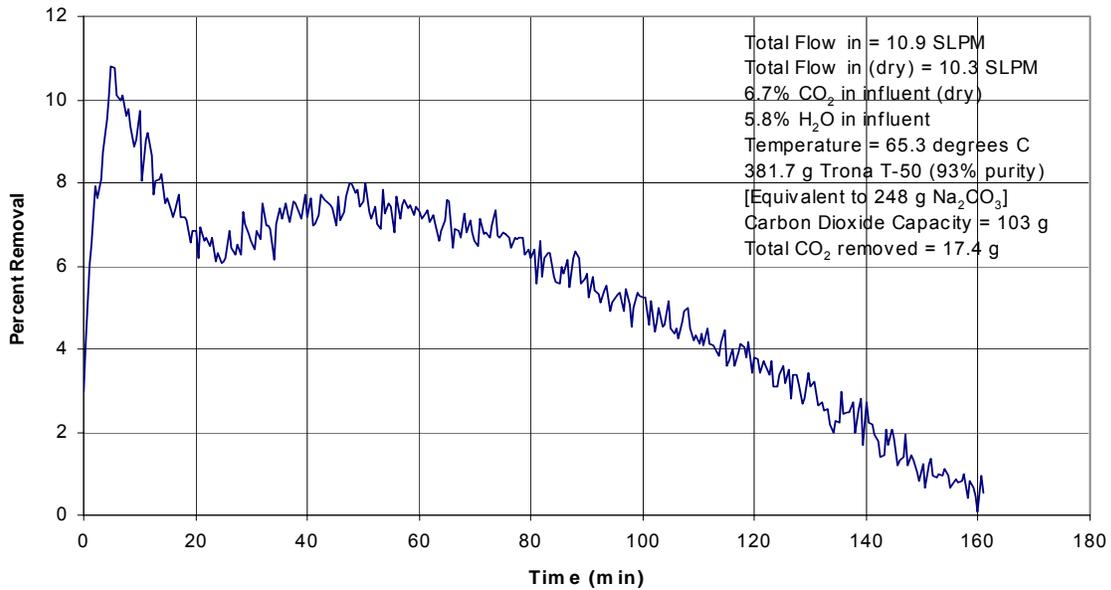


Figure 50. Cycle 2 carbonation test with Trona T-50

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 Two-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
Exposure Time (min)	180	160

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.

3.4.3 Test 3: Potassium Carbonate: 1 cycle

Several unsuccessful attempts were made to conduct cyclic fluidized-bed tests using potassium carbonate as a sorbent. Problems were encountered with plugging of the bed, as indicated by an increase in differential pressure across the bed. The bed plugged both during pre-drying in dry nitrogen, and during carbonation in nitrogen/oxygen/carbon dioxide/steam mixtures. In general, the material is hygroscopic and tends to agglomerate during storage. A single carbonation cycle was completed during one test. Data are shown in Figure 51. The reactor temperature profile is shown in Figure 52. The reactor plugged up upon calcination following this carbonation cycle.

The test was conducted with 6.55% carbon dioxide and 6.14% water in the inlet gas. Carbon dioxide removal in the early stages of this test peaked at about 35% and remained above 15% for the first 30 minutes. The temperature in the bed increased rapidly due to the exothermic nature of the reaction. The fact that CO₂ removal continued to take place at these temperatures (peaking at about 110°C, averaged across the bed) demonstrates a potential advantage of potassium carbonate over sodium carbonate for flue gas operations. Unsupported potassium carbonate would, however, be much more difficult to handle.

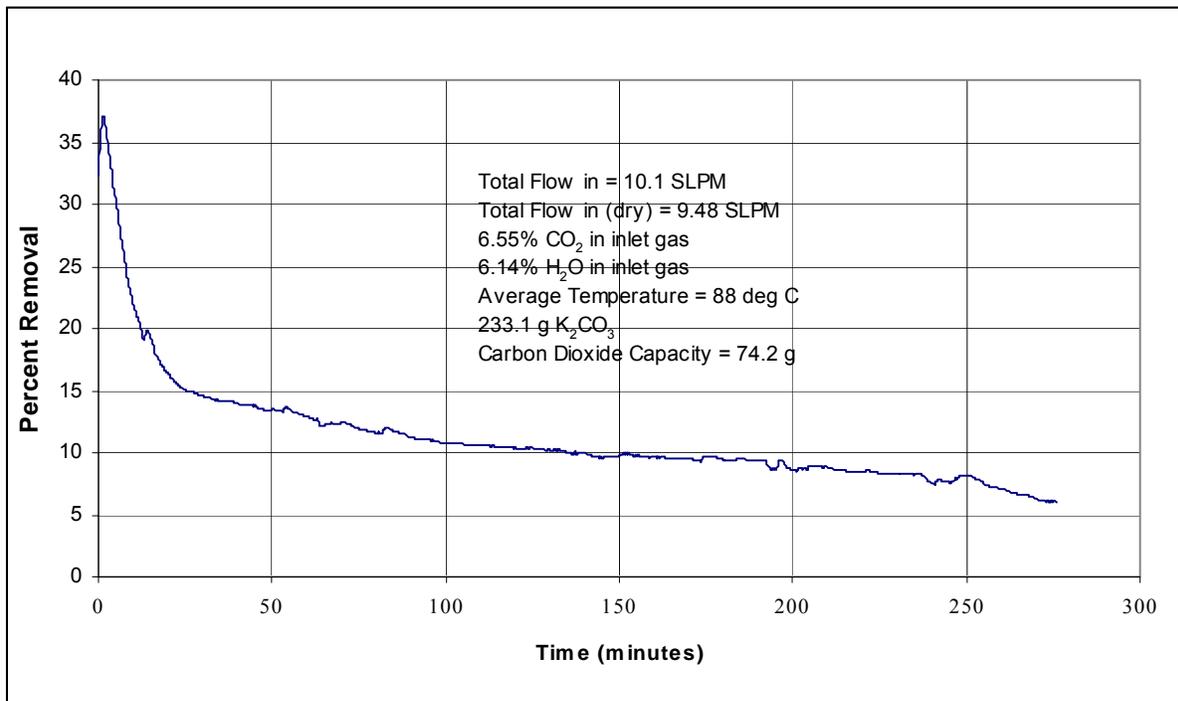


Figure 51. Fluidized-bed carbonation of potassium carbonate (3/11/02)

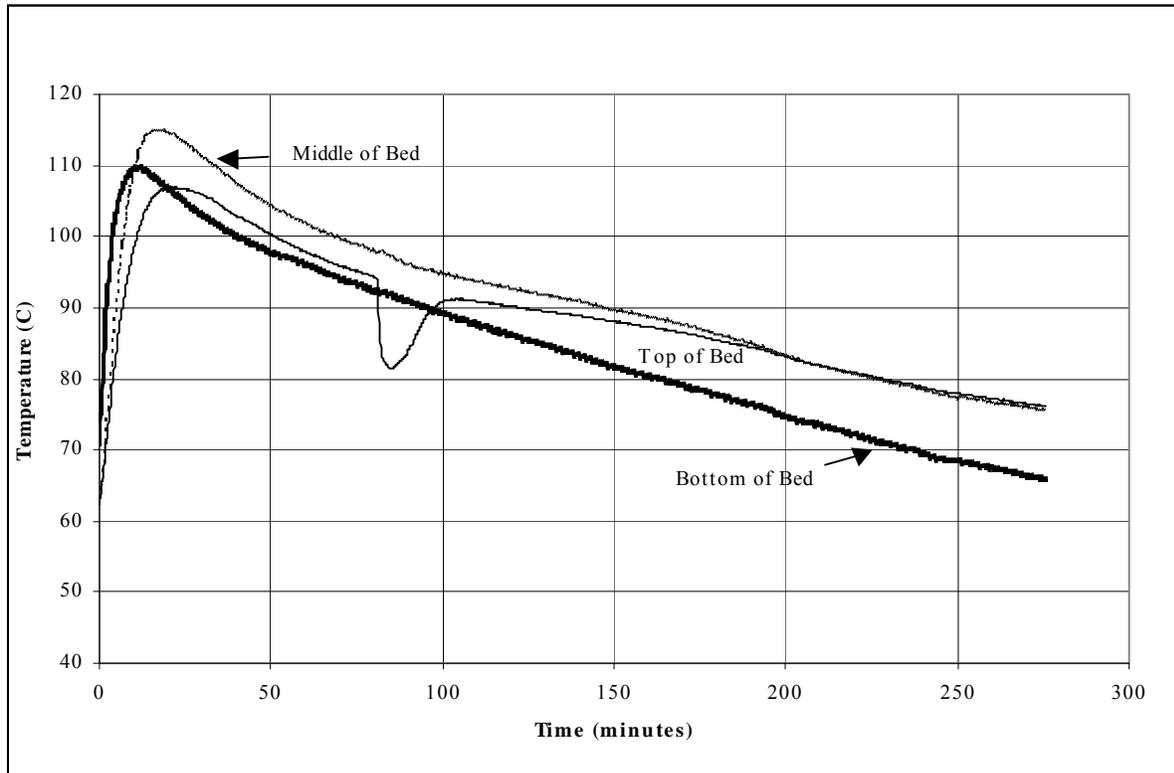


Figure 52. Temperature profile for fluidized-bed carbonation of potassium carbonate

The CO₂ removal declined to about 6% after 280 minutes, at which point the sorbent bed was only 54% exhausted (based on conversion to potassium bicarbonate). The high initial removals may be indicative of reactivity in short residence time reactor systems such as transport reactors or entrained bed systems. On this basis, potassium carbonate may be a promising sorbent if problems related to agglomeration and attrition can be resolved.

3.4.4 Test 4: Trona T-50 (5 cycles)

The reactor was loaded with 406 g of material, and the material was not removed between cycles. This was equivalent to an initial bed height of 6 inches, resulting in a bed height-to-diameter ratio of 3. This mass of trona, after calcination, has a carbon dioxide capacity of 37 g. All calcinations were carried out in nitrogen at 150°C. Carbonation reactions were conducted in a simulated flue gas of 4.7 to 6.5% carbon dioxide and approximately 6.9% water vapor. Carbonation test temperatures varied within the fluidized bed through the course of the cycles, peaking at approximately 75°C. The carbonation cycles were stopped after approximately three

hours, even though most of the stoichiometric capacity of the bed was unused, because the initial rates were of greatest interest. Carbon dioxide removal, and the associated fluidized-bed temperature profiles are shown in Figures 53 through 62. The temperatures at the "bottom," "middle," and "top" of the bed were measured at 1 inch, 3 inches, and 5 inches above the flow distributor. A summary of these data is given in Table 3.

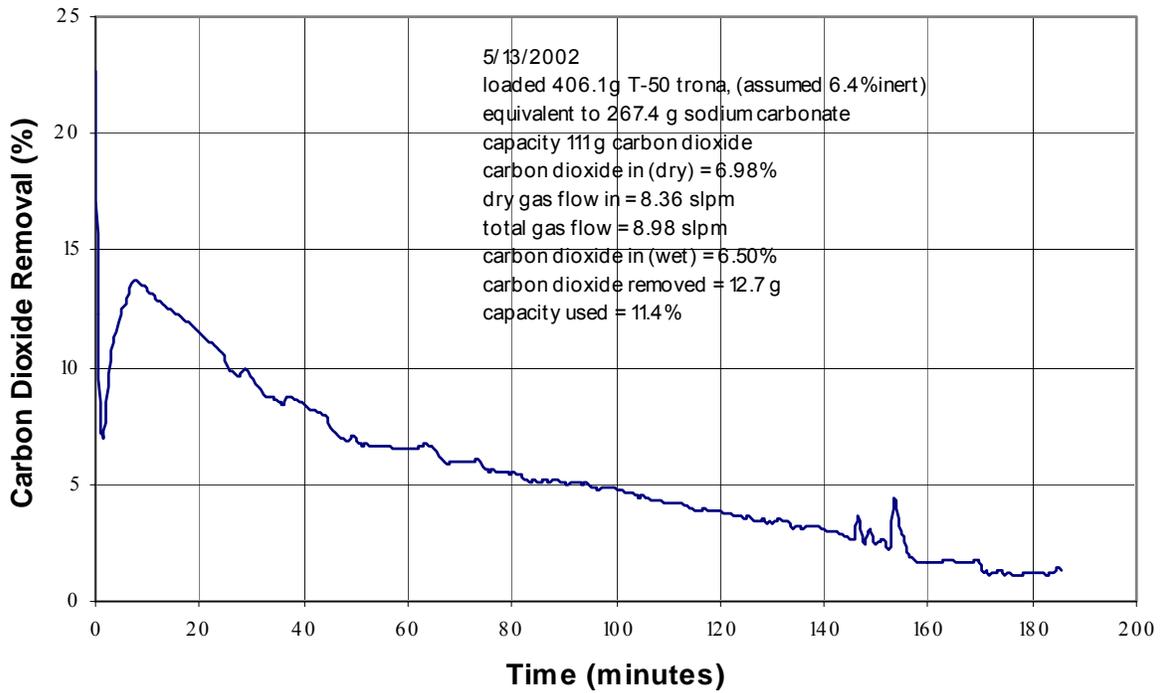


Figure 53. Carbon dioxide removal and trona Cycle 1 - 5/13/2002

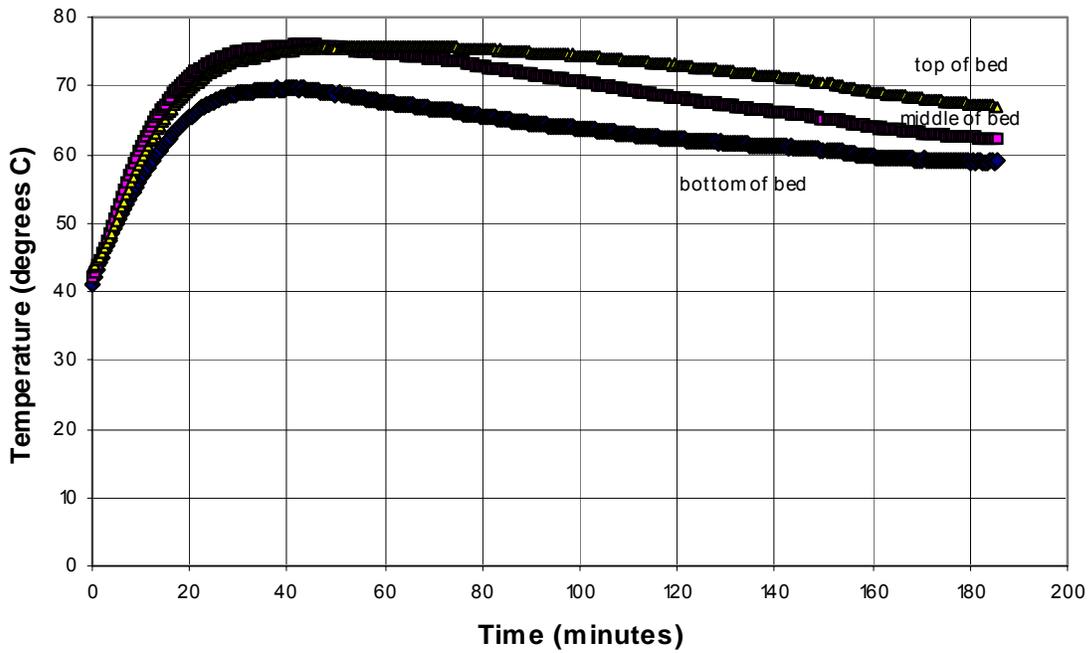


Figure 54. Temperature profile - carbonation Cycle 1 - 5/13/2002

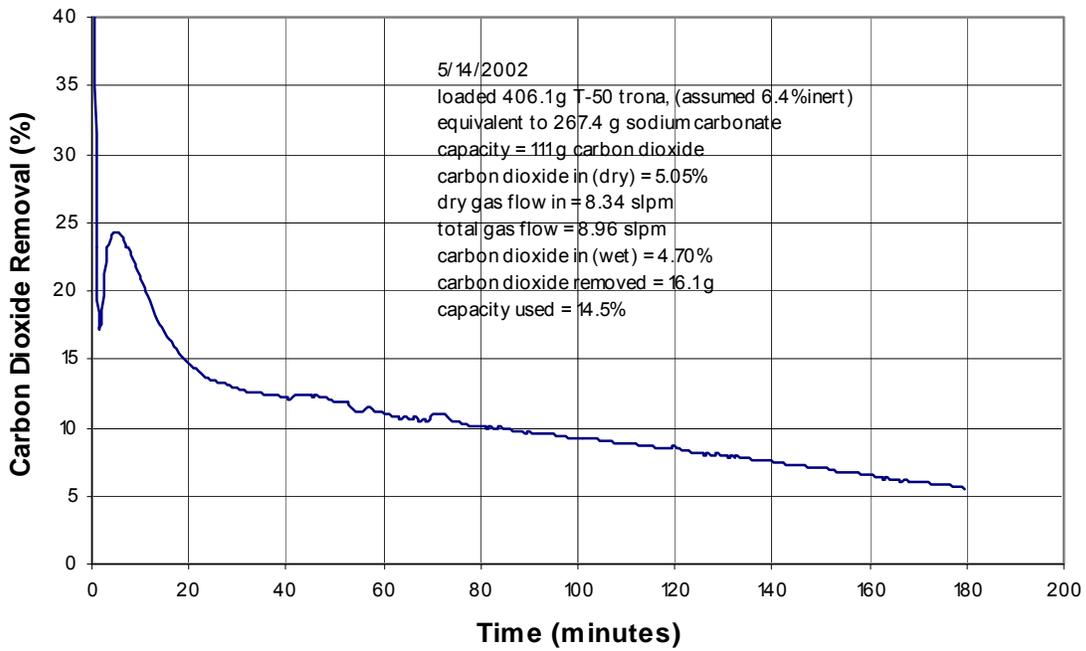


Figure 55. Carbon dioxide removal with trona - Cycle 2 - 5/14/2002

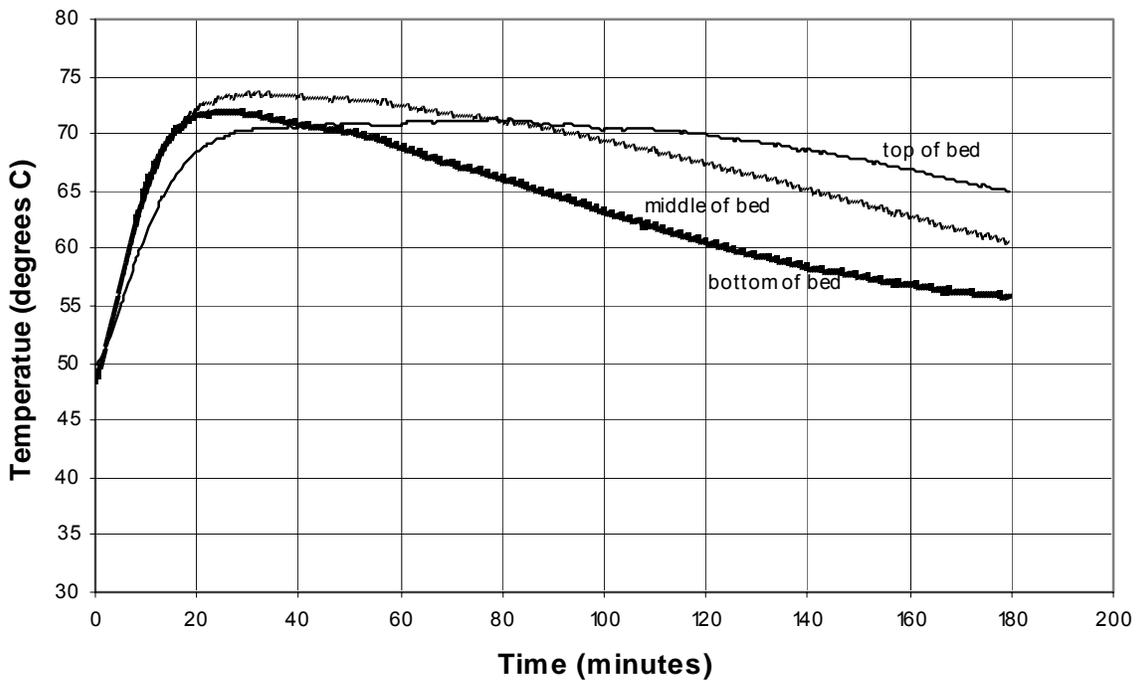


Figure 56. Temperature profile - carbonation Cycle 2 - 5/14/2002

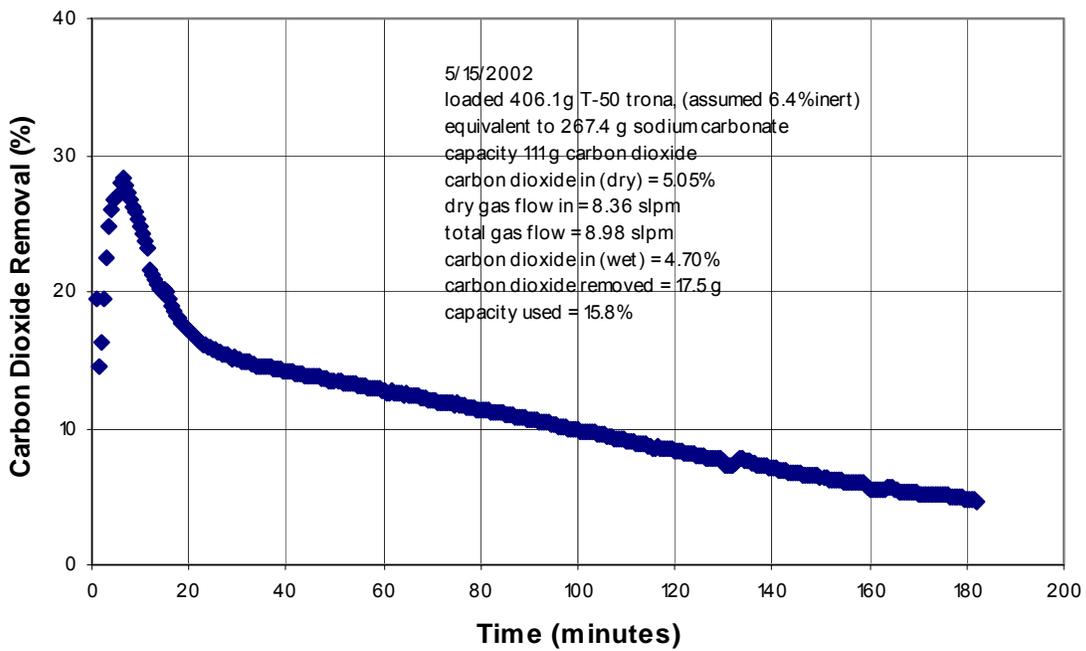


Figure 57. Carbon dioxide removal with trona - Cycle 3 - 5/15/2002

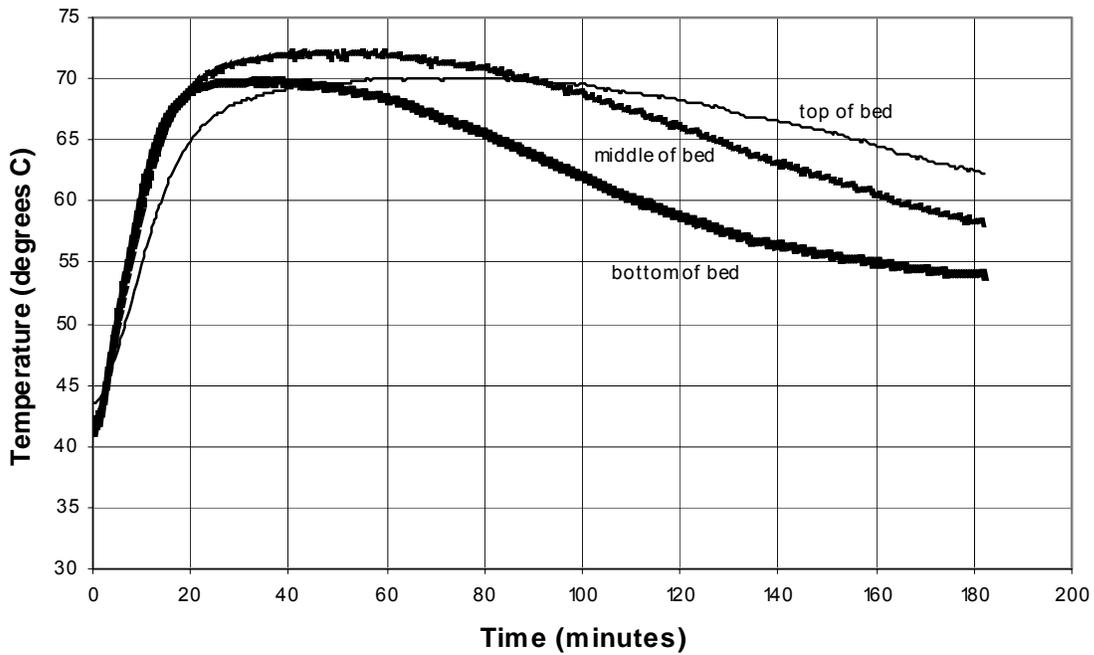


Figure 58. Temperature profile - carbonation Cycle 3 - 5/15/2002

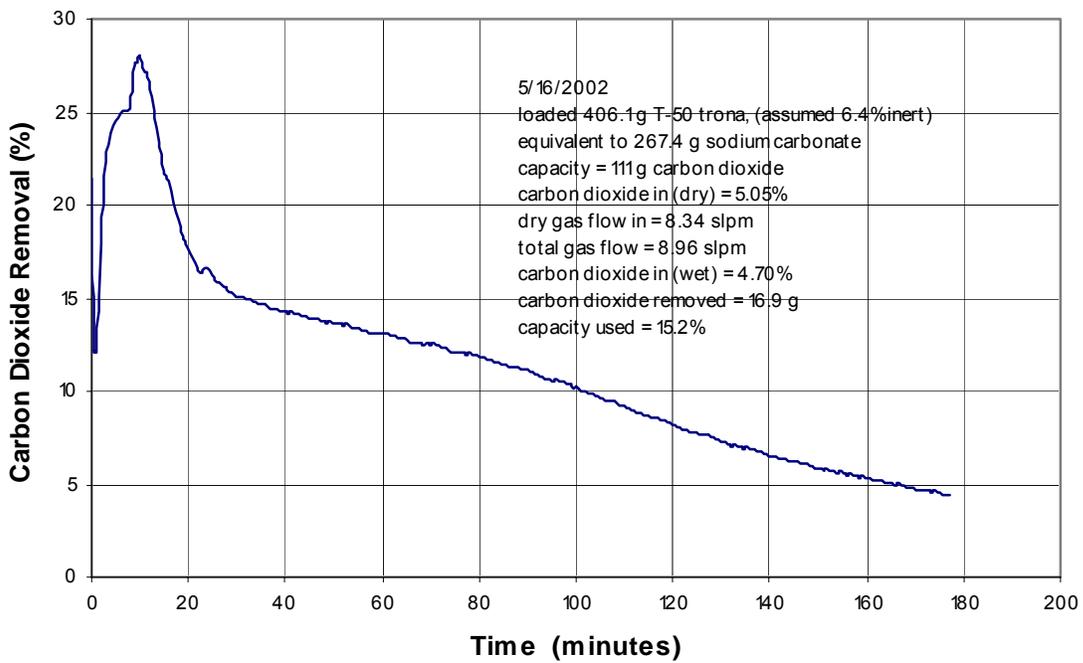


Figure 59. Carbon dioxide removal with trona - Cycle 4 - 5/16/2002

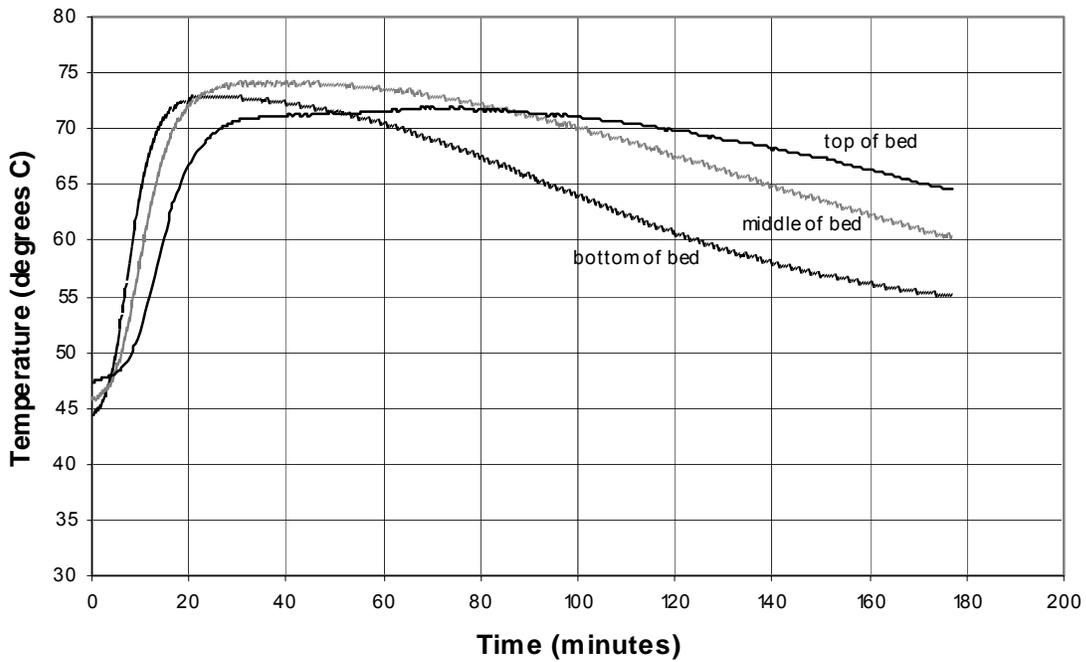


Figure 60. Temperature profile - carbonation Cycle 4 - 5/16/2002

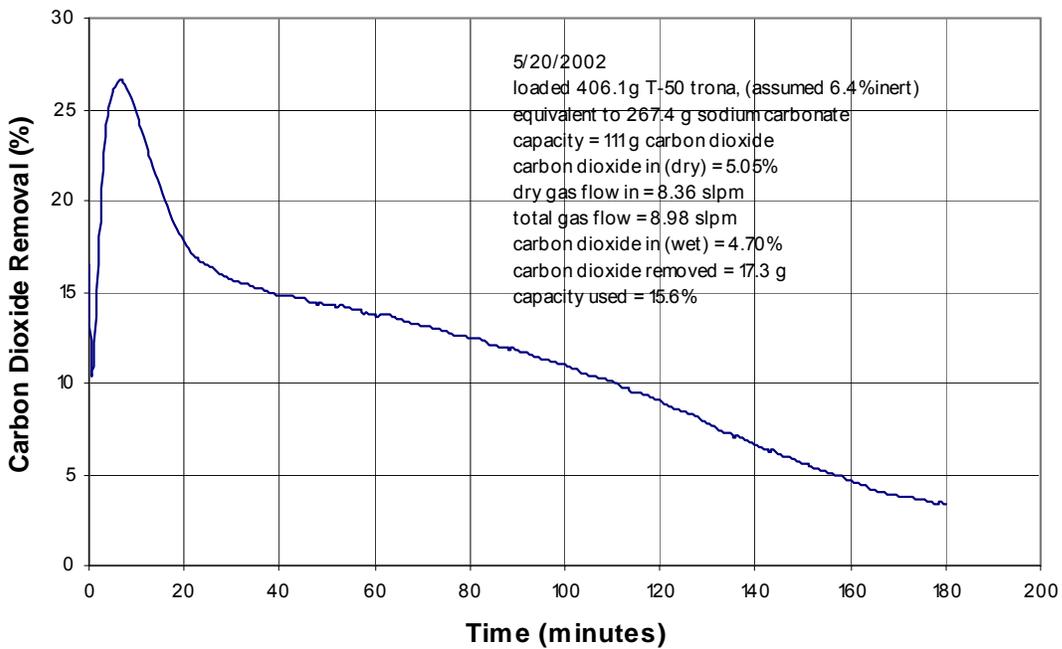


Figure 61. Carbon dioxide removal with trona - Cycle 5 - 5/20/2002

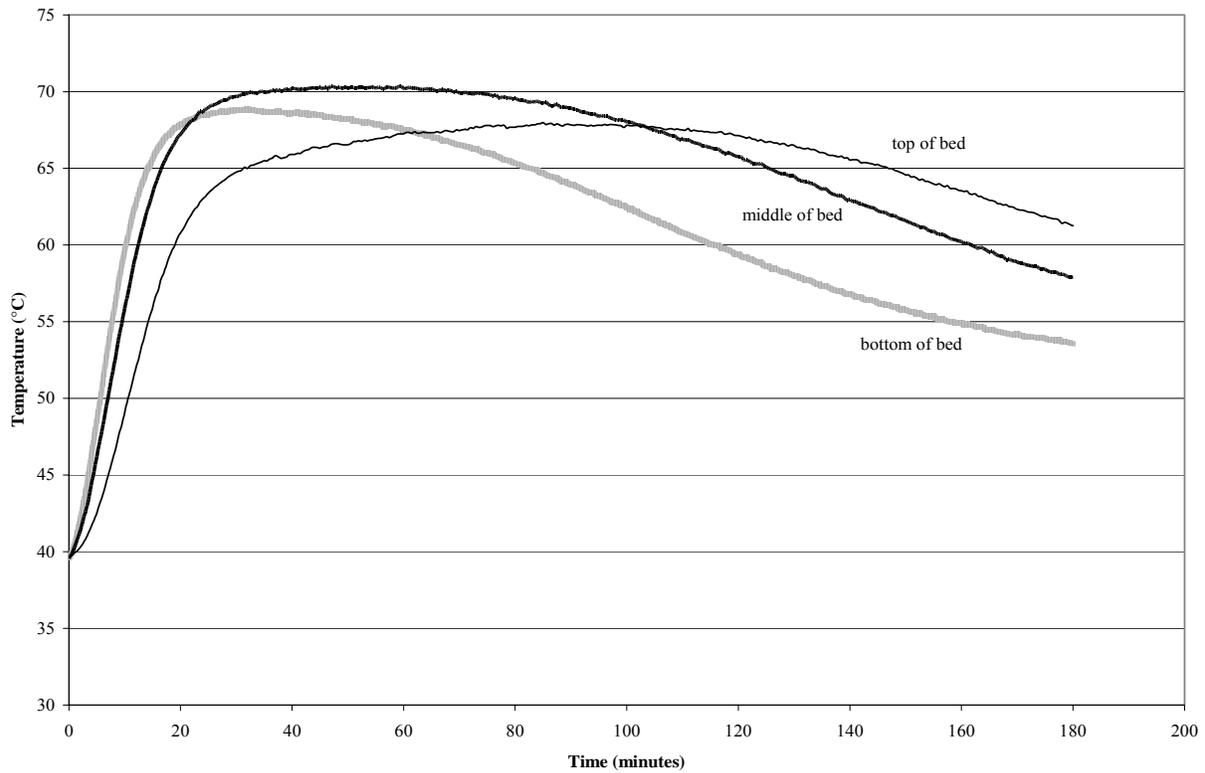


Figure 62. Temperature profile - carbonation Cycle 5 - 5/20/2002

Table 3. Carbon Dioxide Removal in Test 4 (Five-cycle Fluidized Bed Test Using Trona T-50 as Sorbent Precursor)

Cycle	1	2	3	4	5
Total Gas Flow (SLPM)	8.98	8.96	8.98	8.96	8.98
CO ₂ in (%)	6.98	4.70	4.70	4.70	4.70
H ₂ O in (%)	6.90	6.90	6.90	6.91	6.90
CO ₂ removed (g)	12.7	16.1	17.5	16.9	17.3
Capacity used (%)	11.4	14.5	15.8	15.2	15.6

The results are relatively consistent from cycle to cycle with no indication that the activity of the sorbent declined over the course of the five cycles. Variations in temperature are unavoidable with strongly exothermic reactions in the present well-insulated reactor system. The initial removal rates of 15 to 30 percent, as shown in the data for the first 15 to 30 minutes of the run, are more significant than the overall sorbent capacity usage over the three-hour duration.

3.4.5 Test 5: Spray-Dried 40% Supported Potassium Carbonate (5 Cycles)

A second five-cycle fluidized-bed test was conducted using a spray-dried 40% potassium carbonate on alumina support. This material was tested because of its superior attrition resistance to granular potassium carbonate, and because the support provides a heat sink for the energy released by the carbonation reaction. Experimental conditions were similar to the previous test. The reactor was loaded with 379 g of sorbent, and the material was not removed between cycles. This was equivalent to an initial bed height of 5.5 inches. The potassium carbonate content of this sorbent has a carbon dioxide capacity of 48.2 g (assuming conversion to bicarbonate). All calcinations were carried out in nitrogen at 150°C. Carbonation reactions were conducted in a simulated flue gas of 6.28% carbon dioxide and approximately 6.2% water vapor. Carbonation test temperatures varied within the fluidized bed through the course of each cycle, peaking at approximately 105°C. The carbonation cycles were stopped after 3 to 3.5 hours, even though most of the stoichiometric capacity of the bed was unused, because the initial rates are of greatest interest. Carbon dioxide removal, and the associated fluidized-bed temperature profiles are shown in Figures 63 through 72. The temperatures at the "bottom," "middle," and "top" of the bed were measured as in the trona tests. A summary of these data is given in Table 4.

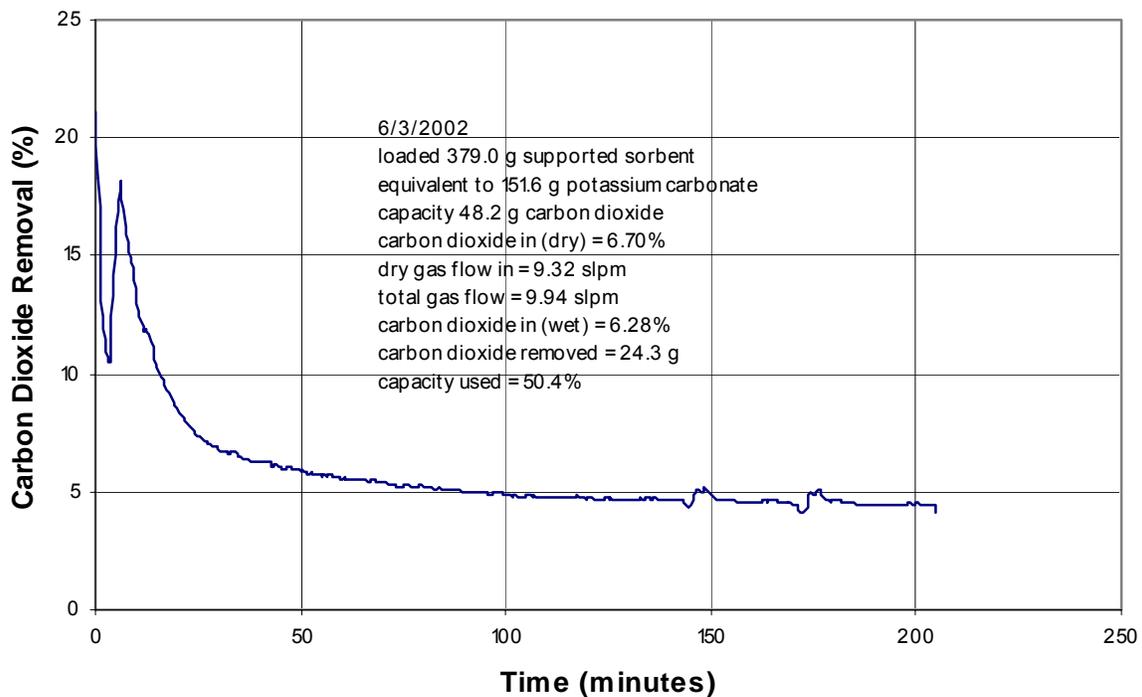


Figure 63. Fluidized-bed carbonation of 40% supported potassium carbonate - Cycle 1

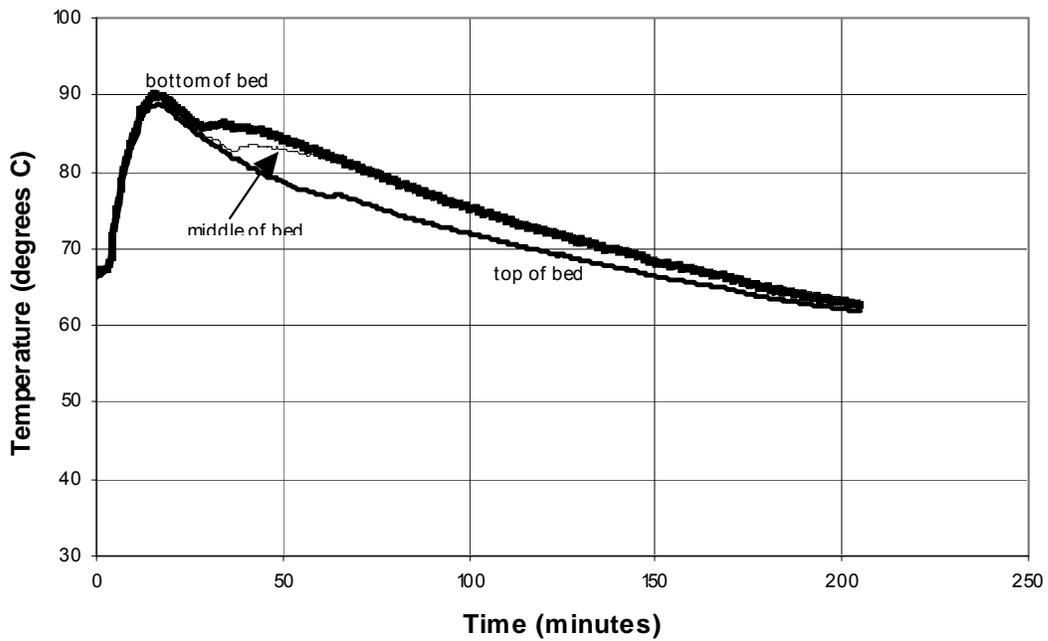


Figure 64. Temperature profile - 40% supported potassium carbonate - Cycle 1

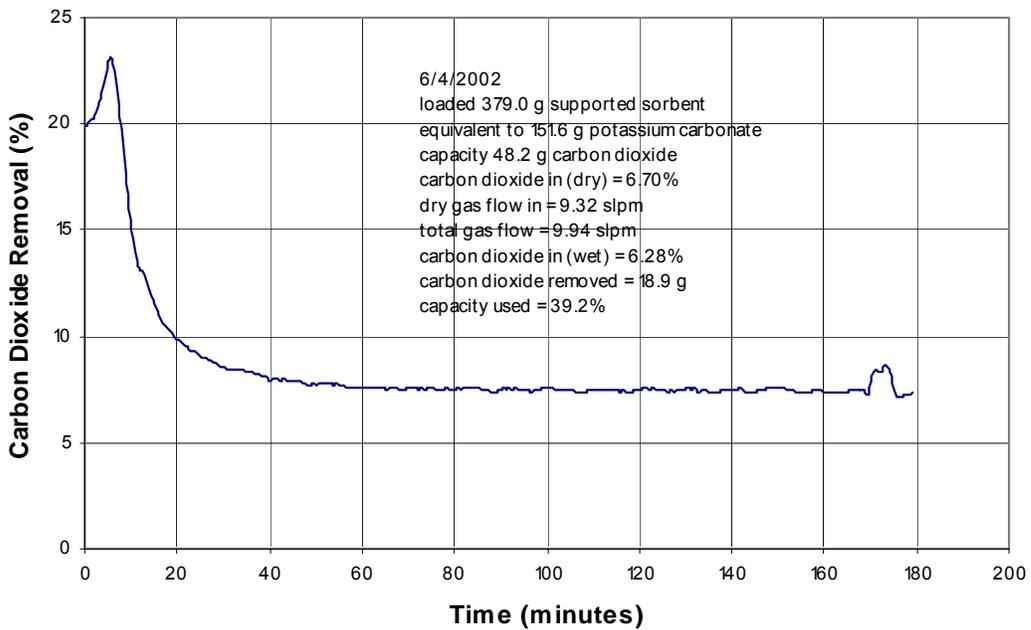


Figure 65. Fluidized-bed carbonation of 40% supported potassium carbonate - Cycle 2

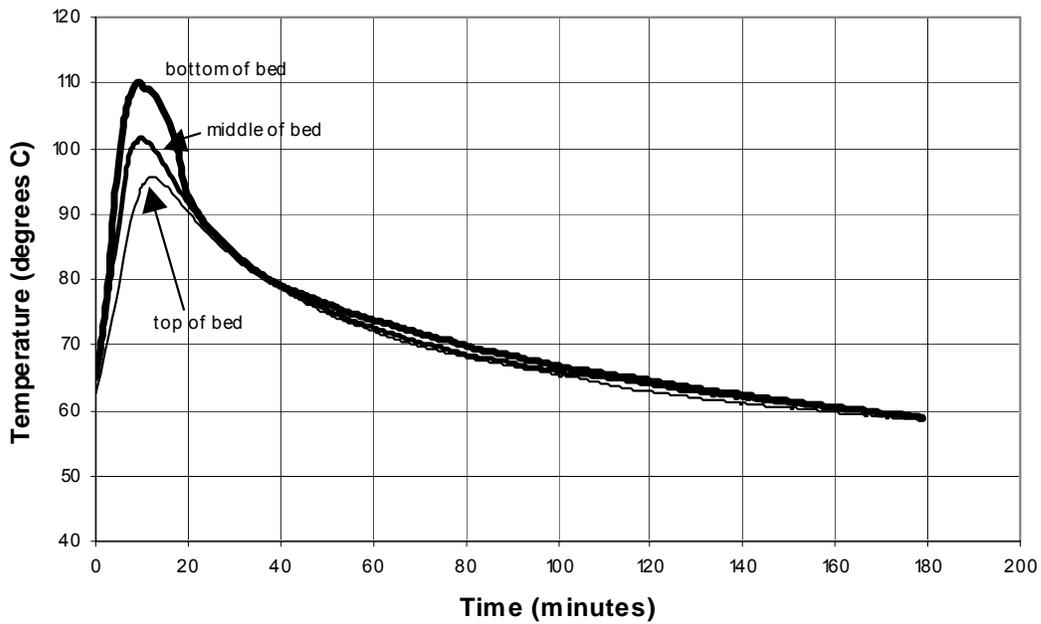


Figure 66. Temperature profile - 40% supported potassium carbonate - Cycle 2

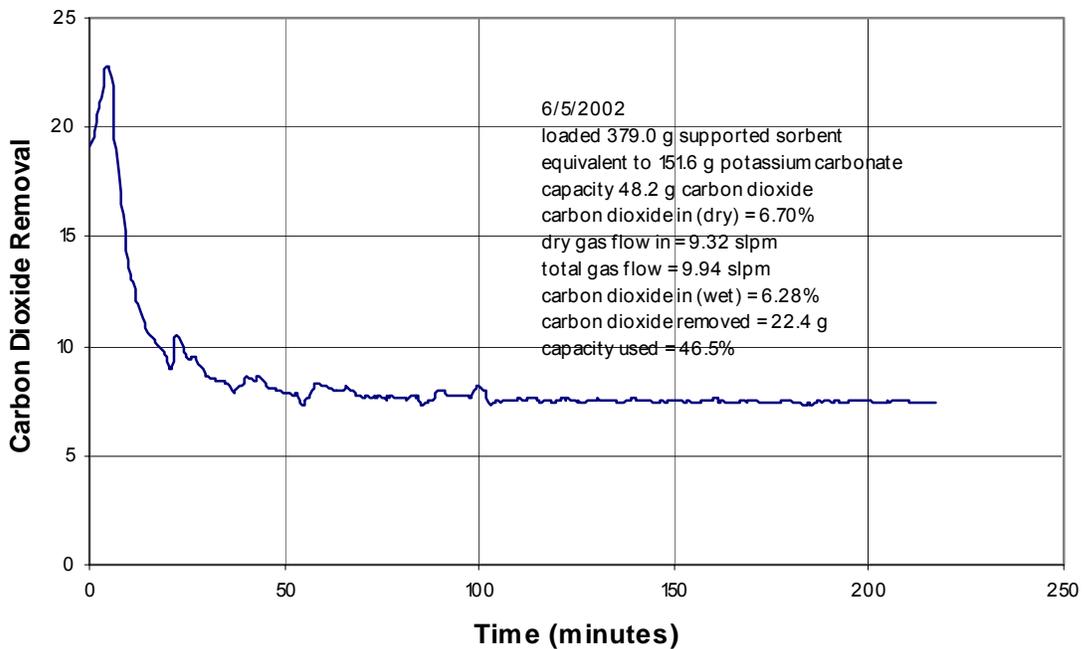


Figure 67. Fluidized-bed carbonation of 40% supported potassium carbonate - Cycle 3

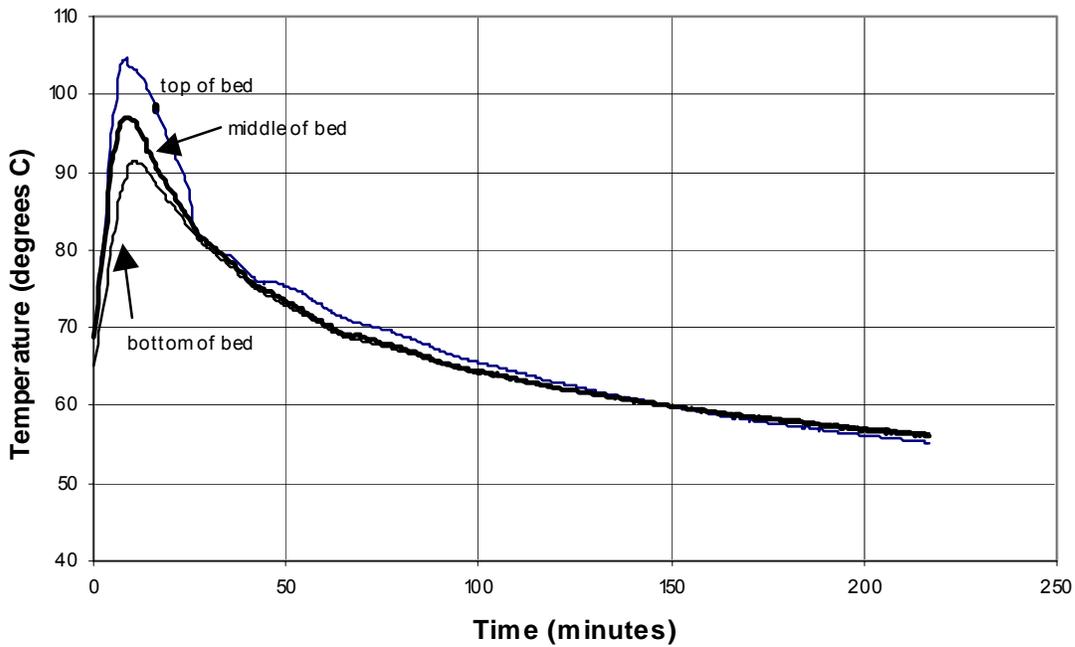


Figure 68. Temperature profile - 40% supported potassium carbonate - Cycle 3

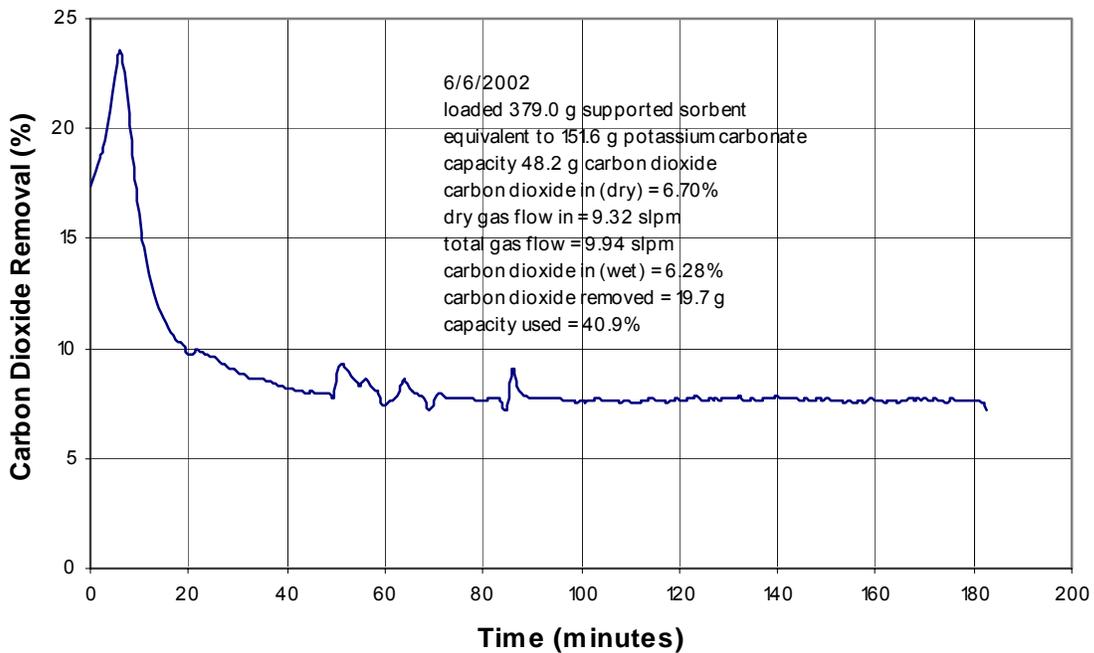


Figure 69. Fluidized-bed carbonation of 40% supported potassium carbonate - Cycle 4

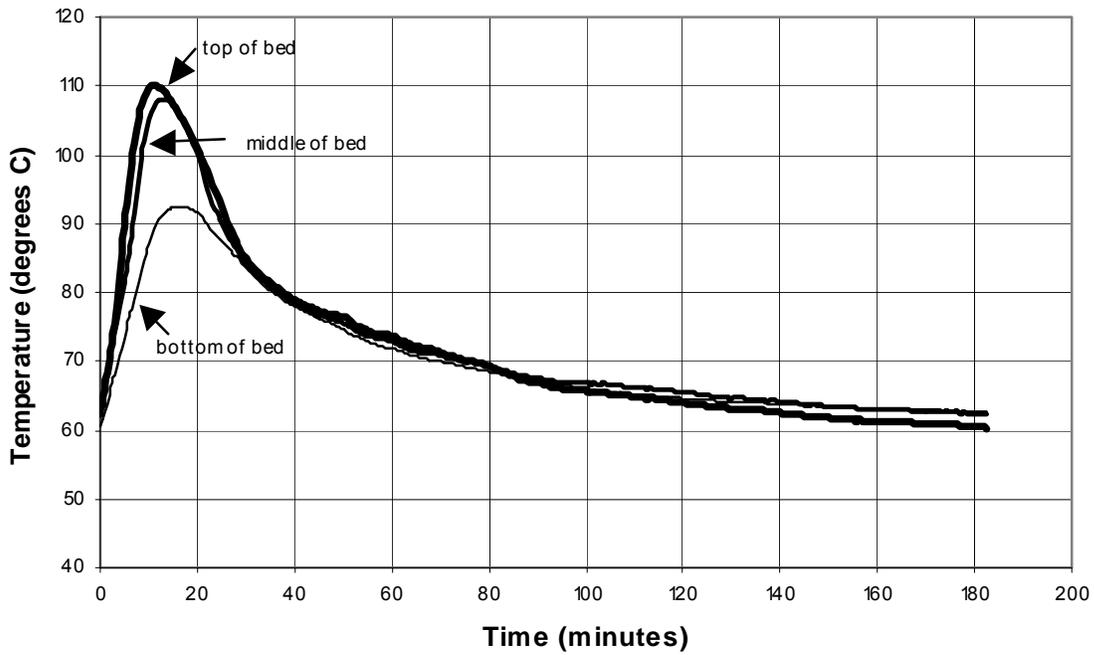


Figure 70. Temperature profile - 40% supported potassium carbonate - Cycle 4

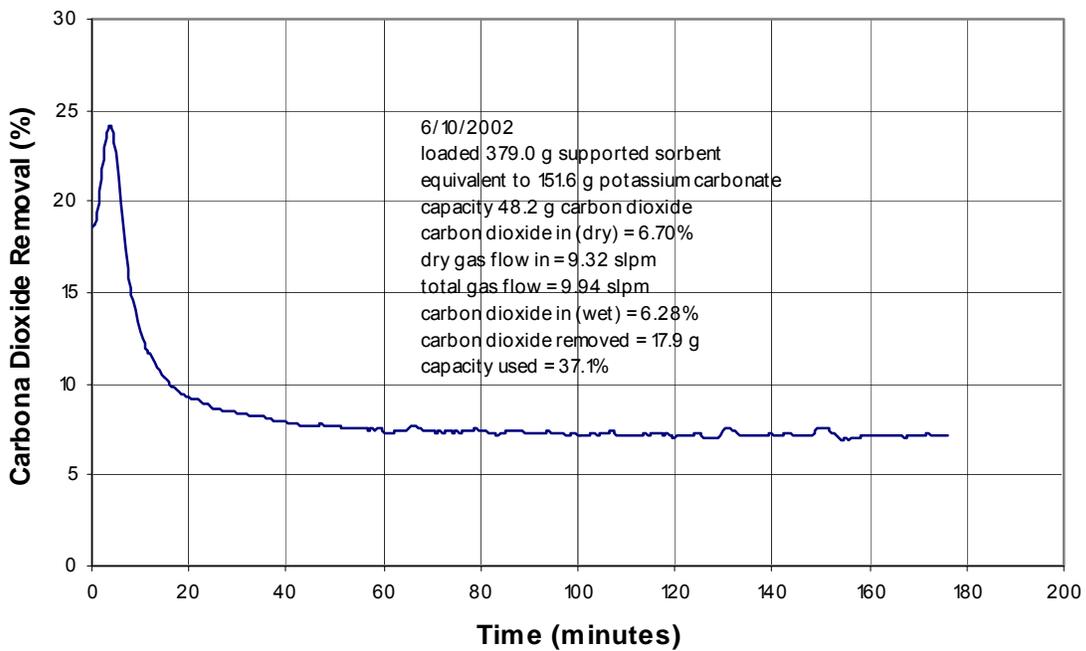


Figure 71. Fluidized-bed carbonation of 40% supported potassium carbonate - Cycle 5

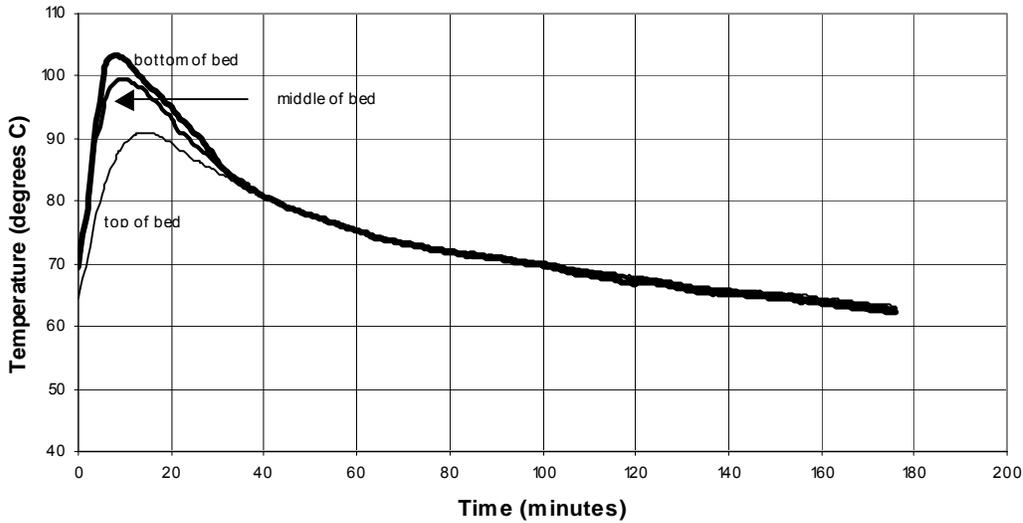


Figure 72. Temperature profile - 40% supported potassium carbonate - Cycle 5

Table 4. Carbon Dioxide Removal in Test 5 (Five-cycle Fluidized-Bed Test Using Spray Dried Supported Potassium Carbonate)

Cycle	1	2	3	4	5
Total Gas Flow (slpm)	9.94	9.94	9.94	9.94	9.94
CO ₂ in (%)	6.28	6.28	6.28	6.28	6.28
H ₂ O in (%)	6.24	6.24	6.24	6.24	6.24
CO ₂ removed (g)	24.3	18.9	22.4	19.7	17.9
Capacity used (%)	50.4	39.2	46.5	40.9	37.1

3.4.6 Test 6: 10% Supported Potassium Carbonate (5-cycles)

The reactor was loaded with 190 g of sorbent material, which contained 19 g of potassium carbonate and 171 g of support material. The carbon dioxide capacity of the sorbent, assuming complete conversion of potassium carbonate to potassium bicarbonate (and no activity due to the support material) was 6.0 g. Integration of the carbon dioxide removal data indicated that greater than 100% of the stoichiometric capacity of the potassium carbonate was used, suggesting that the support was reversibly adsorbing carbon dioxide. Carbonation cycles were extended for 3 hours, as in past tests. Useful data were obtained from three carbonation cycles; experimental problems occurred in the first and third cycles. The carbon dioxide concentration

at the reactor exit, as well as the sorbent bed temperature rise, suggested that the reaction was essentially complete within the first few minutes of each carbonation cycle. Data for the second, fourth, and fifth cycles are shown in Figures 73 through 81.

The data suggest a rapid reaction rate. While the reactivity of the support, which makes up 90% of the sorbent material, complicates data analysis (making it impossible to derive a quantitative reaction rate) the temperature rise in the sorbent bed confirms that a rapid exothermic reaction is taking place.

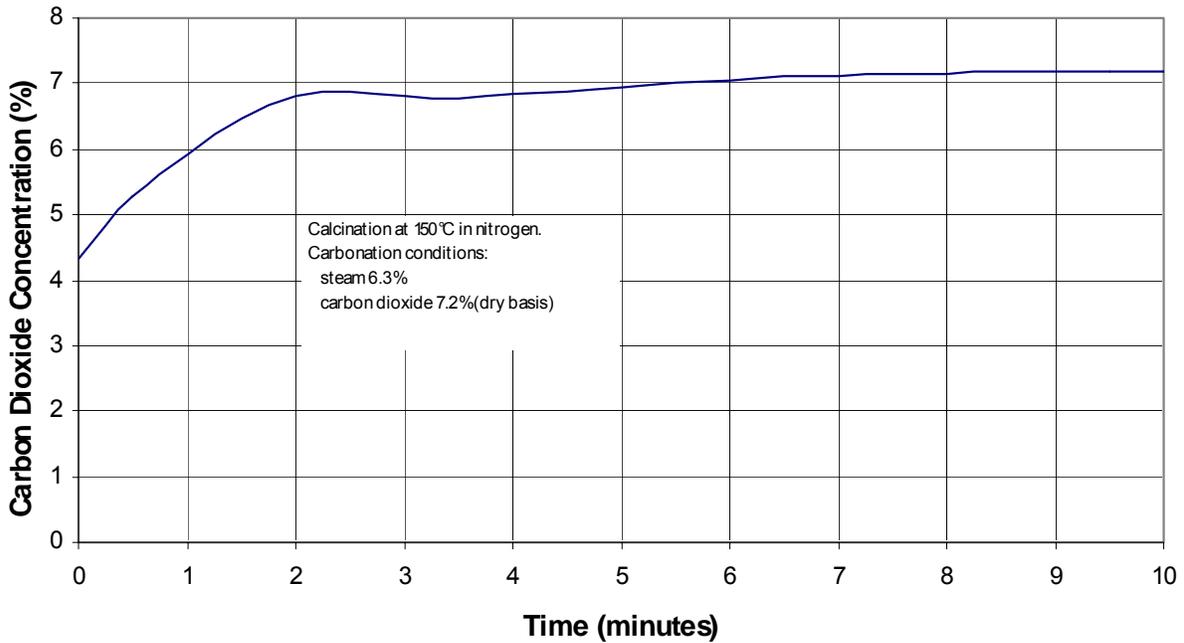


Figure 73. Test data from carbonation cycle

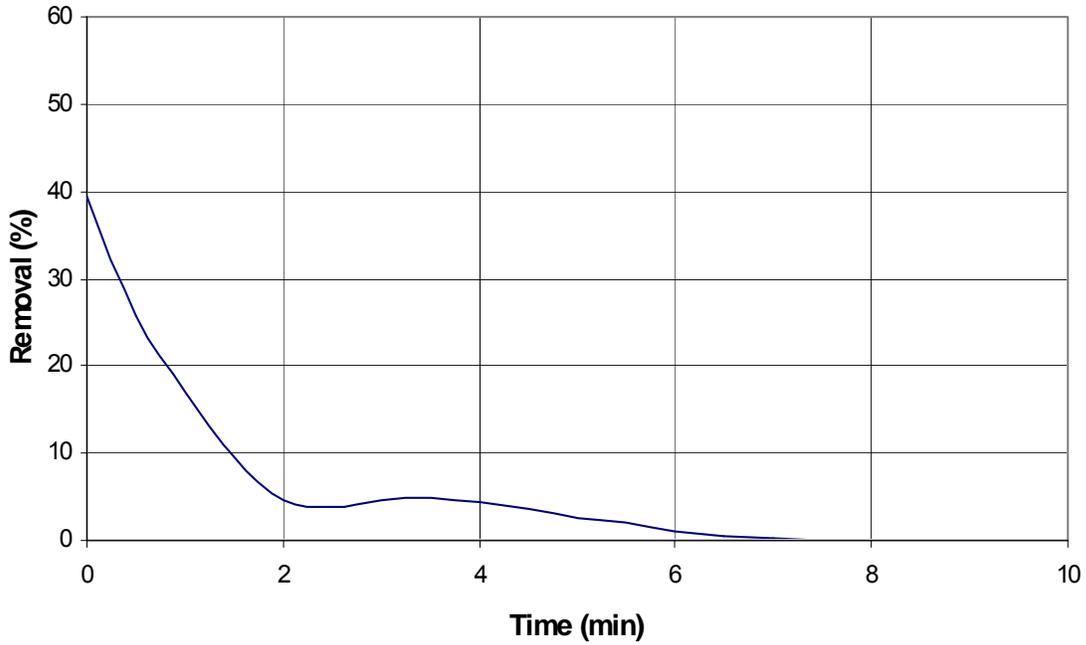


Figure 74. Test data from carbonation Cycle 2 with 10% supported potassium carbonate sorbent - CO₂ removal

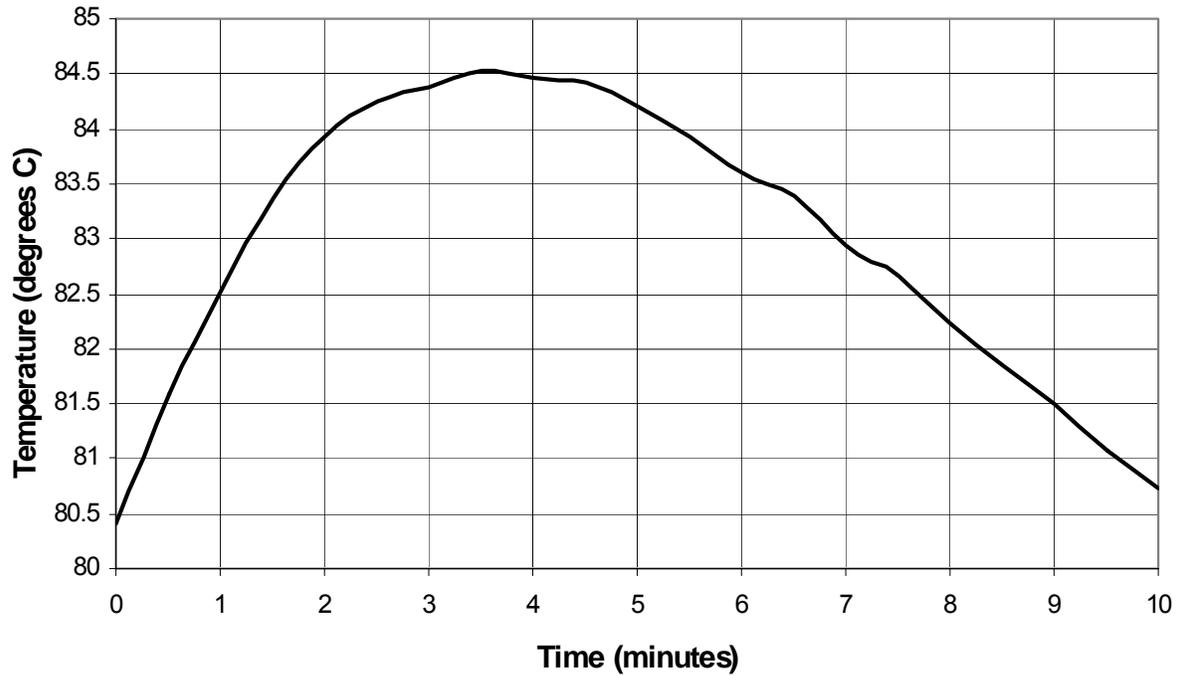


Figure 75. Test data from carbonation Cycle 2 with 10% supported potassium carbonate sorbent - average bed temperature

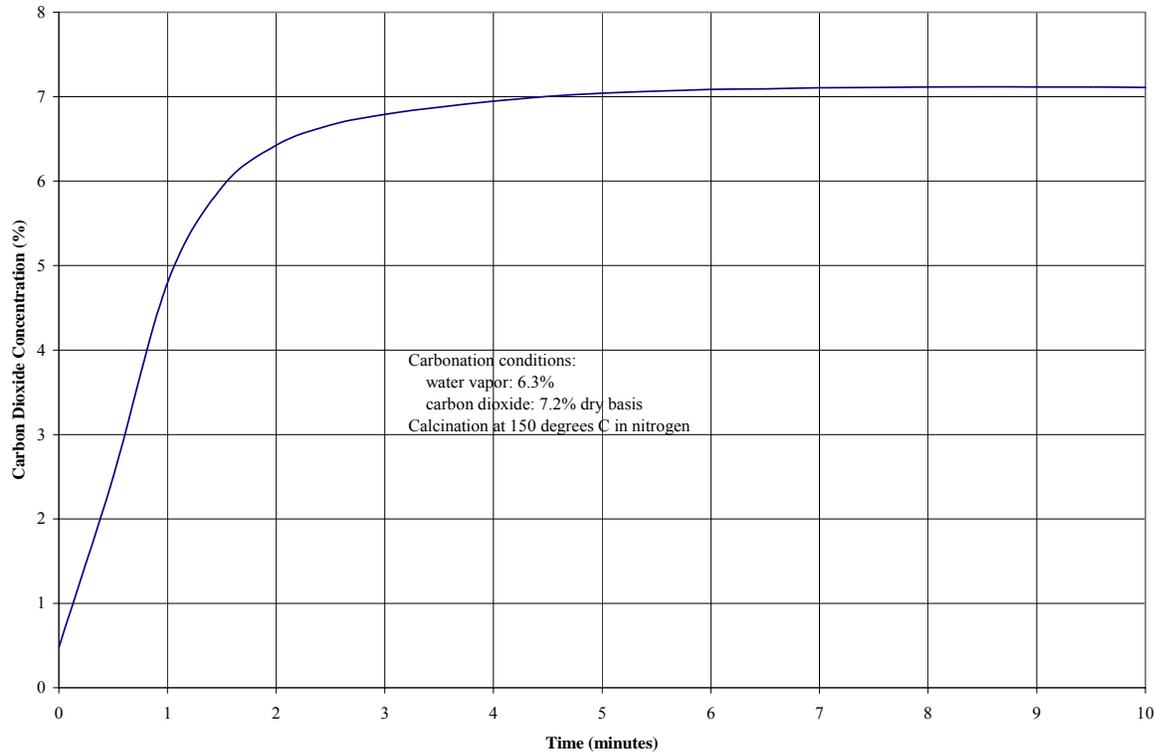


Figure 76. Test data from carbonation Cycle 4 with 10% supported potassium carbonate sorbent - CO₂ concentration in reactor exit gas

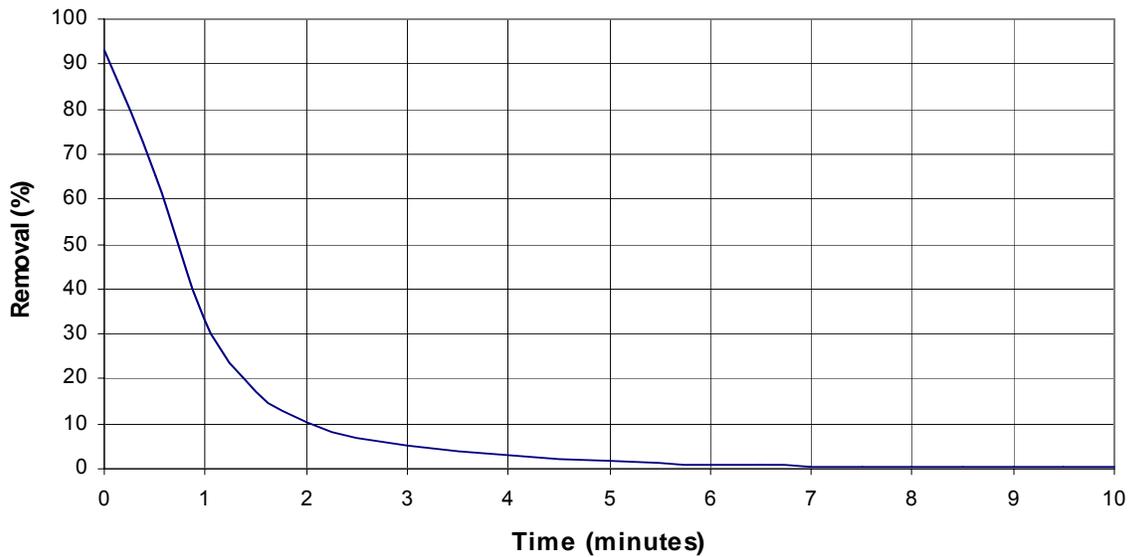


Figure 77. Test data from carbonation Cycle 4 with 10% supported potassium carbonate sorbent - CO₂ removal

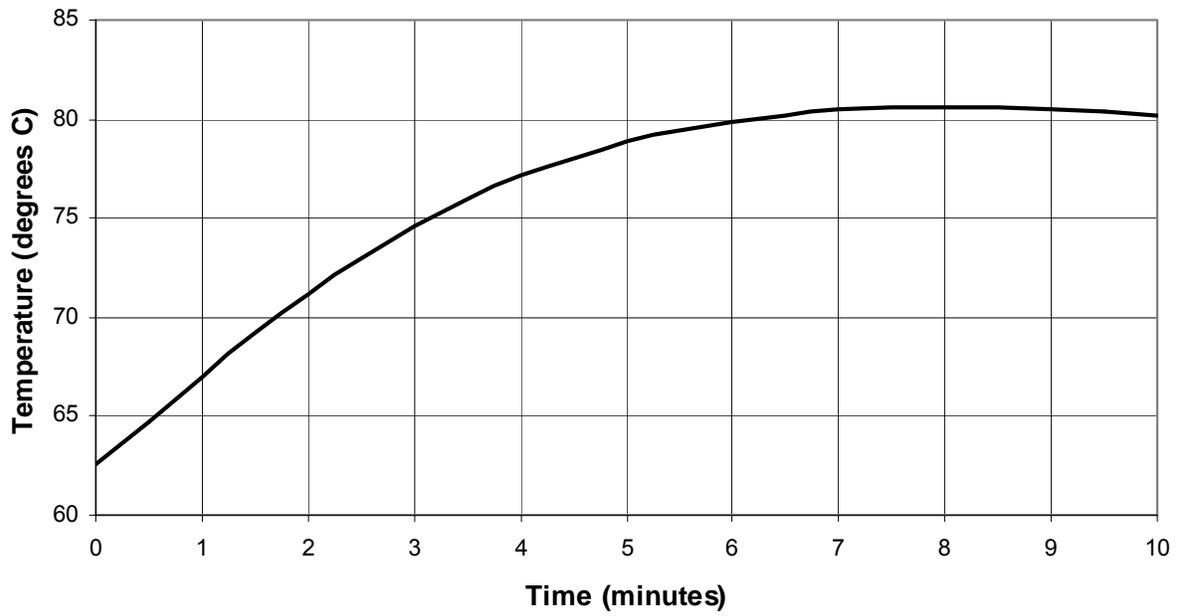


Figure 78. Test data carbonation Cycle 4 with 10% supported potassium carbonate sorbent - average bed temperature

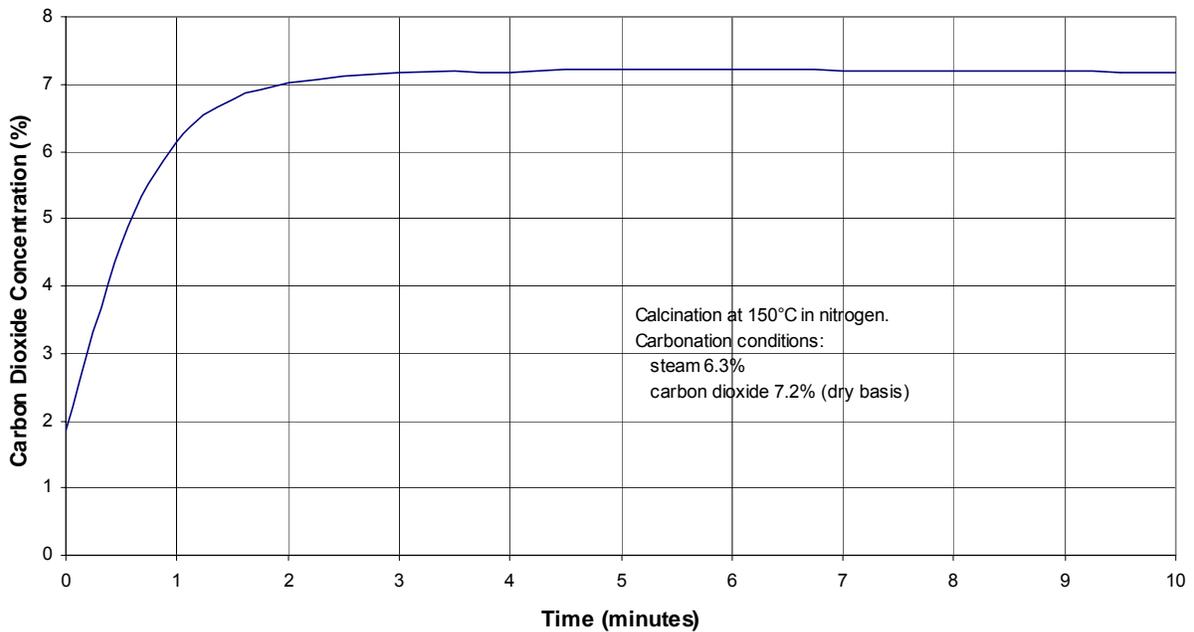


Figure 79. Test data from carbonation Cycle 5 with 10% supported potassium carbonate sorbent - CO₂ concentration in reactor exit gas

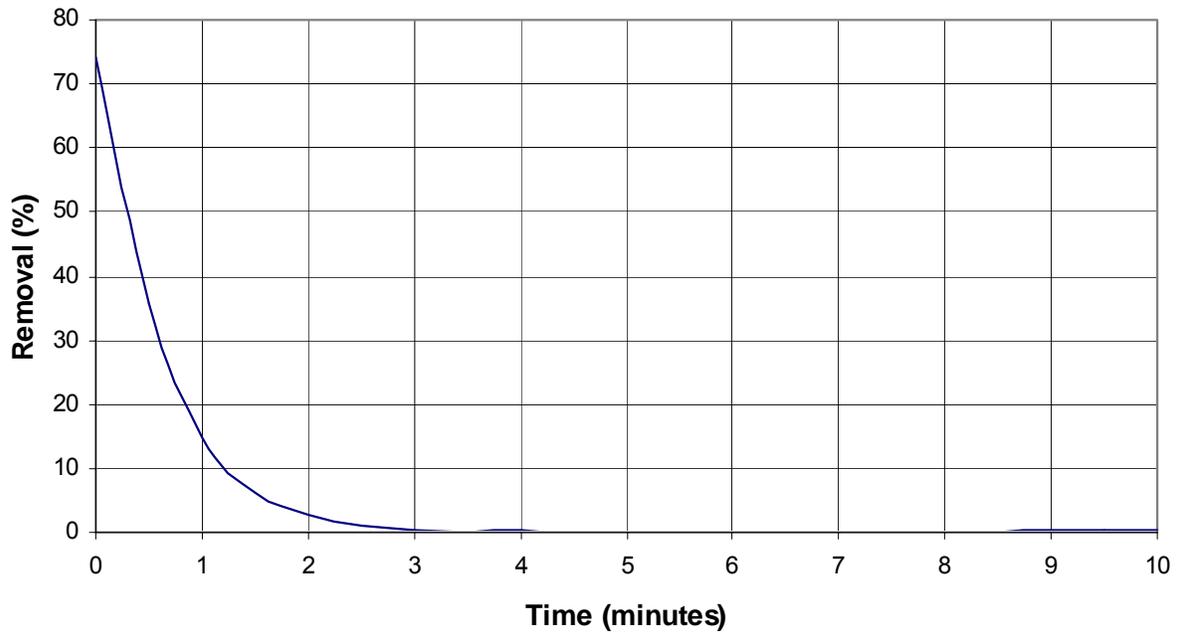


Figure 80. Test data from carbonation Cycle 5 with 10% supported potassium carbonate sorbent - CO₂ removal

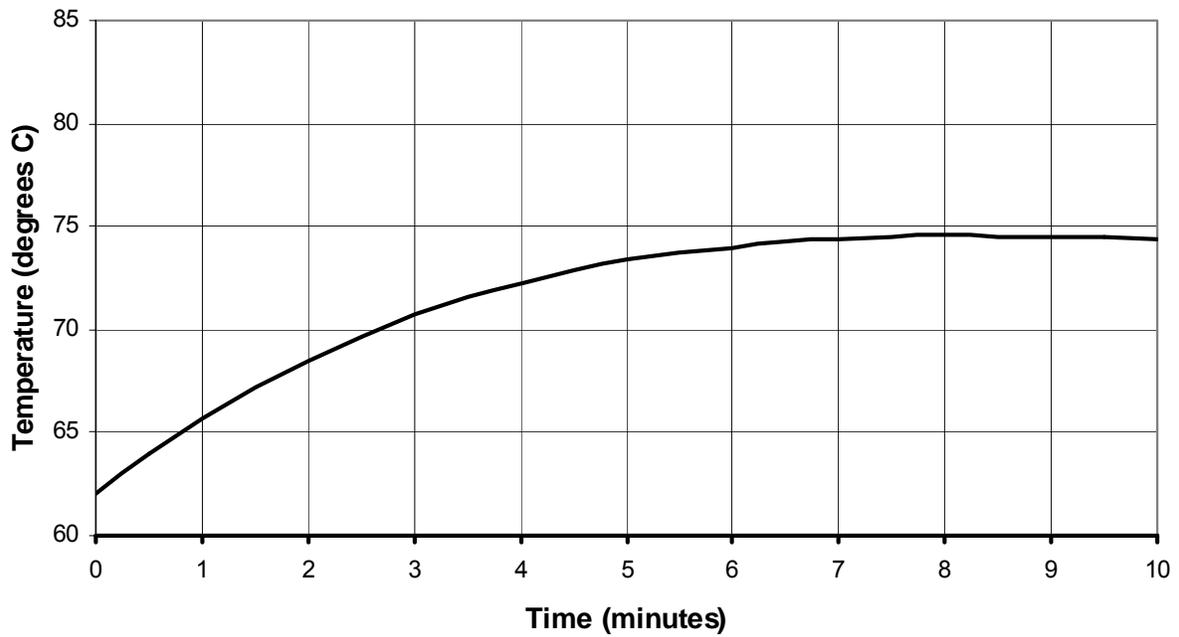


Figure 81. Test data from carbonation Cycle 5 with 10% supported potassium carbonate sorbent - average bed temperature

3.5 PROPERTIES OF UNSUPPORTED SORBENTS AND SORBENT PRECURSORS

RTI measured particle size, BET surface area, porosity, ASTM attrition index, and bulk density of selected samples of the unsupported sorbents tested. The various grades of SBC and trona were tested before and after laboratory calcination. Properties of sodium bicarbonate (SBC) materials and trona are given in Table 5 and 6 respectively. Structural properties such as pore volume and particle size of these materials appear suitable for use. However, the ASTM attrition index of these materials is very high. Typical ASTM attrition index of an attrition-resistant material such as FCC is 0.2-0.5. Except for SBC grade 5, all of the materials tested appear to exhibit poor attrition resistance. However the large particle size and narrow size distribution of the SBC grade 5 is unsuitable for use in a transport reactor.

3.6 CHARACTERIZATION AND TESTING OF SUPPORTED MATERIALS

RTI produced a series of sorbents composed of sodium carbonate incorporated in a ceramic support. Two potassium carbonate materials used for fluidized bed testing were also prepared. The objective of the sorbent development work was to produce an active (as indicated by high BET surface area and rapid conversion to Wegscheider's salt) material which is mechanically stable (as indicated by a high value for compact bulk density and a low value for the attrition ration (AR) based on the Davison test). Sorbent composition and spray dryer operation were varied to identify important parameters.

The compositions and selected properties of these materials are shown in Table 7. This table also includes the properties of calcined SBC#3 and those of plain support materials, without incorporation of Na_2CO_3 . TGA weight gains based on a 20-minute exposure to an atmosphere of 7.5% carbon dioxide and 5.9% water vapor at 60°C were used to compare carbonation activity of the different sorbents.

The goal of the supported sorbent development program is to produce a sorbent that is more active than calcined SBC#3, with attrition resistance comparable to that of commercial FCC materials. These requirements must be satisfied for a transport reactor system to be effectively used for this reaction cycle. A transport reactor process involves a short residence time (on the order of 5-10 seconds) and requires a material which will be mechanically stable over many (typically more than 100) carbonation/calcination cycles.

Table 5. Physical properties of Sodium Bicarbonate Materials

		SBC grade 1 fresh	SBC grade 1 calcined overnight at 125°C in air	SBC grade 2 fresh	SBC grade 2 calcined overnight at 125°C in air	SBC grade 3 fresh	SBC grade 3 calcined 3 hours at 125°C in air	SBC grade 3 calcined overnight at 125°C in air	SBC grade 5 fresh	SBC grade 5 calcined 3 hours at 125°C in air
Particle Size Distribution (%)										
297	microns	0	0	0	0.65	0	n/a	0	0	n/a
-297+177	microns	0	0	0	0.98	0	n/a	0.65	27.7	n/a
-177+125	microns	0	0	8.61	8.82	0	n/a	0	63.85	n/a
-125+88	microns	8.56	8.7	65.56	64.38	1.03	n/a	0.98	5.74	n/a
-88+75	microns	19.86	20.4	13.58	13.07	0.69	n/a	1.31	0	n/a
-75+53	microns	43.84	41.47	8.28	9.15	10.31	n/a	10.46	1.35	n/a
-53	microns	27.74	29.43	3.97	2.94	87.97	n/a	86.6	1.35	n/a
mean particle size	microns	60.7	60.2	100.2	104.4	31.6	n/a	33.3	169.4	n/a
harmonic mean	micron	48.6	47.9	89.4	92.3	28.6	n/a	28.9	150.2	n/a
BET Surface Area	sq. m/g	1.348	2.537	5.167	2.435	3.748	3.462	2.686	4.1	2.093
Mercury Porosimetry Data										
Total Intrusion Volume	ml/g	0.0454	0.3908	0.0295	0.3562	n/a	0.5389	0.775	n/a	0.1138
Total Pore Area	m ² /g	5.688	14.68	6.574	12.383	n/a	12.064	20.195	n/a	7.066
Median Pore Diameter	(vol) Å	76426	3531	10389	3320	n/a	65260	51357	n/a	3425
Median Pore Diameter	(area) Å	51	72	53	87	n/a	62	63	n/a	59
Average Pore Diameter	(4V/A) Å	320	1065	179	1150	n/a	1787	1532	n/a	644
Bulk Density	g/ml	1.8389	1.185	2.0798	1.3447	n/a	0.8359	0.7089	1.12	1.8198
Apparent Density	g/ml	2.0065	2.2071	2.2157	2.5807	n/a	1.521	1.5695	n/a	2.2954
Porosity	%	8.3578	46.3107	6.1337	47.8928	n/a	45.0432	54.8322	n/a	20.7177
Stem Volume Used	%	10	42	6	40	n/a	54	52	n/a	26
Attrition Index (ASTM)		2.29	n/a	7.55	n/a	4.97	n/a	n/a	0.49	n/a
Bulk Density	lb/ft ³	n/a	n/a	n/a	n/a	n/a	n/a	n/a	69.7	n/a

n/a = not tested

Table 6. Physical Properties of Trona

		Trona T-50 fresh	Trona T-50 calcined overnight at 125°C in air	Trona T-200 fresh	Trona T-200 calcined overnight at 125°C in air	Sodium Carbonate (commercial grade)
Mercury Porosimetry Data						
Total Intrusion Volume	ml/g	0.0294	0.2517	0.3481	0.7056	n/a
Total Pore Area	m ² /g	7.3	9.4	14.9	11.7	n/a
Median Pore Diameter	(vol) Å	7410	2833	68950	49258	n/a
Median Pore Diameter	(area) Å	42	100	41	91	n/a
Average Pore Diameter	(4V/A) Å	162	1074	938	2415	n/a
Bulk Density	g/ml	2.03	1.58	1.17	0.84	n/a
Apparent Density	g/ml	2.16	2.63	1.97	2.08	n/a
Porosity	%	6	39.8	40.6	59.3	n/a
Stem Volume Used	%	8	44	48	70	n/a
Attrition Index (ASTM)		1.79	n/a	7.95	n/a	2

n/a = not tested

Table 7. Supported Sorbent Characterization

Sample #	Na₂CO₃ content of sorbent (%)	Compact Bulk Density (g/mL)	BET Surface Area (sq. m/g)	TGA Weight Gain, 20 min. (%)	Attrition Ratio (AR)
041604-1a	0	0.68	96.6	3.8	3.1
042004-1a	0	0.74	120.8	4.6	3.0
040204-1a	20	0.51	28.43	7	Nt
040504-1a	40	0.64	12.91	10	Nt
040804-1a	20	0.5	33.7	6.2	Nt
040904-1a	40	0.64	14.29	9	Nt
041204-1a	20	0.5	31.4	6.6	Nt
041604-2a	40	0.64	13.5	8.7	Nt
041604-3a	50	0.71	10.7	9.2	Nt
042104-1a	40	0.74	7.9	8.9	Nt
042104-2a	40	0.74	7.0	7.9	Nt
042804-1a	20	0.43	34.8	6.7	Nt
042804-2a	40	0.51	10.9	8.9	Nt
042904-1a	40	0.49	9.84	9.1	Nt
050504-3	40	0.89	6.96	5.2	1.3
050704-1a	40	0.54	14.3	nt	2.3
050704-3a	40	0.54	11.4	nt	1.3
110102-1	7.5	nt	178	6.0	1.0
K-1 ⁺⁺⁺	40	nt	4.5	nt	nt
K-2 ⁺⁺⁺	10	nt	93	nt	nt
Calcined SBC 3	---	0.99	2.41	4.2	nt
FCC+	---	0.96	nt	nt	1.0
RTI-5	40	1.61	1.85	1.5	0.51

nt = not tested

+ = Commercial fluid cracking catalyst (standard material)

+++ = Potassium Carbonate

As seen in Table 7, sorbents have been developed in the laboratory with substantially greater activity than calcined SBC#3. The increased activity is even more significant when the reduced fraction of active material (typically 40-50% for supported sorbents as opposed to 100% for calcined SBC#3) is considered. Some of these sorbents also exhibit AR of 1.0 to 1.5 indicating that they are attrition resistant. One promising spray-dried material produced at RTI containing 40% Na₂CO₃ that had relatively high carbonation activity and good attrition resistance was selected for scale-up. A commercial catalyst manufacturer prepared several hundred pounds of this material (RTI-5). The commercially produced material had excellent attrition resistance but had very low reactivity. A review of the procedures used to produce this material suggested that there were significant differences in the production technique between the laboratory and the scale-up facility. Another attempt to scale up this material or a similar formulation is planned.

CHAPTER 4

CONCLUSIONS

This study has demonstrated the technical feasibility of a dry, regenerable, sodium sorbent-based process for the capture of CO₂ from flue gas, and the production of pure CO₂ suitable for use or sequestration during the sorbent regeneration phase. The process offers a potential alternative to amine-based scrubbing processes for CO₂ capture from flue gas.

CO₂ capture is accomplished by the reversible reaction with Na₂CO₃ to form either NaHCO₃ or Wegscheider's salt, depending on reaction conditions. The reaction is reversed at higher temperature to regenerate the sorbent and liberate equal molar quantities of CO₂ and H₂O. Pure CO₂ for use or sequestration is produced after condensation of the H₂O. The carbonation (CO₂ capture) reaction is feasible in the temperature range of 60°C to 70°C, with the lower temperature limit established by the dew point of the carbonation feed gas, and the upper temperature limited by the thermodynamics of the exothermic, reversible carbonation reaction. This narrow temperature window coupled with the exothermic nature of the carbonation reaction indicates that careful energy management and temperature control will be required in a commercial process.

A promising means of temperature control of the carbonation reaction is evaporative cooling through the addition of atomized liquid water to the reactor. This is complicated by the tendency of the sorbent materials to cake. Sorbent regeneration in pure CO₂ should be carried out at a temperature of about 160°C. Acid flue gas contaminants such as SO₂ and HCl will react irreversibly with the sorbent to such an extent that an upstream desulfurization process will be required when using sulfur-containing fossil fuels.

CO₂ removal efficiencies of about 90% were achieved during the early stages of laboratory-scale fixed-bed and fluid-bed reactor tests. Complete carbonation of the sorbent was possible when the fixed-bed tests were carried out to completion. No deterioration in sorbent performance occurred in 15-cycle fixed-bed tests.

The calcination reaction, which regenerates the sorbent for reuse, has been confirmed to go to completion in laboratory-scale reactor systems. This endothermic reaction is responsible for most of the process energy requirements. While this heat requirement is fixed by the heat of

reaction, the economic feasibility of the process will be improved by using the lowest quality heat available from the power plant.

Capital and operating costs will be strongly affected by the reactivity and attrition resistance of the sorbent. A faster and more complete carbonation will result in smaller and less expensive contacting equipment. Sorbents with greater attrition resistance will result in reduced sorbent loss and thus lower operating cost. Supported sorbent have been prepared in the laboratory with increased reactivity as well as increased attrition resistance. Scale up of these sorbents to large quantity is in progress.

CHAPTER 5

FUTURE WORK

5.1 MATHEMATICAL MODELING OF THE PROCESS

Using ASPEN PLUS process simulation software, a model has been developed to represent a cyclic sodium carbonate sorbent-based, entrained-bed reactor process to capture and concentrate carbon dioxide from flue gas. This model will be refined to produce realistic material and energy balances, optimizing the use of heat from the power plant for sorbent regeneration. Ultimately, this model will be used to size equipment for a full-scale process. Capital and operating cost estimates will then be developed for the process.

5.2 PILOT-SCALE TESTING

Several multicycle tests will be conducted at a pilot-scale entrained-bed reactor facility. These tests will be conducted in single-loop mode with sorbent from the carbonation reaction collected and reloaded for calcination. The results of these tests will provide a good estimate of the rates that can be expected in a full-scale transport reactor system and will impact reactor sizing and economic feasibility analyses.

5.3 SORBENT DEVELOPMENT

Work will continue in the laboratory spray dryer system to produce active, attrition-resistant sorbents that can be scaled to large-quantity production.

CHAPTER 6

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