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Carbon dioxide capture from flue gas using regenerable sodium-based sorbents

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CARBON DIOXIDE CAPTURE FROM FLUE GAS USING REGENERABLE SODIUM-BASED SORBENTS

A Thesis

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering in The Department of Chemical Engineering

by

Ya Liang
B.S., Tsinghua University, 1999
August, 2003
To

My Parents
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Abstract

The overall objective of this project is to develop a simple and inexpensive process to separate carbon dioxide (CO₂) as an essentially pure stream from a fossil fuel combustion gases using a regenerable sodium-based sorbent. This objective of this phase of the project is to evaluate CO₂ capture using sodium-based sorbents in single-cycle and multicycle tests as a function of calcination and carbonation conditions. The sorbent precursors investigated were sodium bicarbonates supplied by Church and Dwight, Inc., and natural trona supplied by Solvay. All precursors were first calcined to sodium carbonate and then converted to sodium bicarbonate (NaHCO₃) or Wegscheider’s salt (Na₂CO₃•3NaHCO₃) through reaction with carbon dioxide and water vapor. Both sodium bicarbonate and Wegscheider’s salt are regenerated to sodium carbonate when heated, producing a nearly pure CO₂ stream after condensation of water vapor.

An electrobalance reactor (thermogravimetric analyzer) and a fixed-bed reactor system were used to study the reaction rate and achievable sorbent capacity as a function of carbonation temperature, carbonation gas composition, and calcination temperature and atmosphere. Sorbent reproducibility and durability were studied in multi-cycle tests.

Electrobalance tests show that sodium bicarbonate (SBC) samples had better performance than Trona samples. Lower carbonation temperature (60°C) and higher CO₂/H₂O concentrations resulted in faster reaction rate and larger sorbent capacity. More severe calcination conditions had a more significant negative effect on Trona than SBC sorbents. In addition, a small amount SO₂ (<0.1%) resulted in a cumulative decrease in CO₂ removal capacity with increasing carbonation cycle number.
Results from 1.5-cycle fixed-bed reactor tests indicate that better CO$_2$ removal efficiency for SBC-3 was achieved at a lower carbonation temperature of 60°C, where average prebreakthrough concentrations corresponded to approximately 75% CO$_2$ removal. There was no obvious deterioration with cycle number. Instead, improved performance between cycle 1 and the remaining cycles was clear for SBC Grades 1 and 3 under the reaction conditions investigated. Prebreakthrough CO$_2$ removal (at the third carbonation sample) increased from 63% in cycle 1 to about 90% for the remaining cycles at 60°C carbonation.
1.1 Global Warming and Greenhouse Gases (GHG)

Global warming, believed to be caused by the greenhouse effect, has received increasing attention in recent years. When solar energy is transmitted through the atmosphere, greenhouse gases trap heat radiating from the earth to cause increasing global surface temperature, which is the greenhouse effect. Researchers estimate that the global average surface temperature has increased between 0.6 and 1.0°C during the last 150 years and will increase by 1.4 to 5.8°C from 1990 to 2100 [Berger, 2002]. The warmest year during the last 1200 years was 1998 and the warmest century over the last 1000 years was the twentieth century [Berger, 2002]. Global warming can melt icebergs and expand oceans [Ledley et al., 1999]. The Intergovernmental Panel on Climate Change (IPCC) predicts that the sea level will rise by 0.09 to 0.88 meters from 1990 to 2100 [Berger, 2002], which will result in 25 percent of the world’s population living less than 1.1 meters above sea level [Global Warming, 2002]. Other probable consequences of global warming include droughts, expanding deserts, heat waves, ecosystem disruption, increasingly severe weather, and loss of agriculture productivity [Global Warming, 2002].

Greenhouse gases include carbon dioxide (CO₂), water vapor (H₂O) [Ledley, et al., 1999; Matthews, 1996], ozone (O₃) [Ledley, et. al., 1999], methane (CH₄), nitrous oxide (N₂O), and chlorofluorocarbons (CFCs) [Ledley, et al., 1999; Morrissey and Justus, 1997]. Since the beginning of the industrial period, the concentrations of the anthropogenic greenhouse gases (CO₂, CH₄, N₂O, CFC-11 (CCl₃F) and CFC-12 (CCl₂F₂)), have increased [Ledley, et al., 1999]. Of those gases, CO₂ is the principal
greenhouse gas of interest because of “its large current greenhouse forcing, its substantial projected future forcing, and its long persistence in the atmosphere” [Ledley, et.al, 1999]. The concentration of CO$_2$ in the atmosphere has increased from 280 ppmv in the preindustrial era to about 364 ppmv in 1997 [Ledley, et. al., 1999]. According to observations at Mauna Loa Observatory, Hawaii, CO$_2$ has increased more quickly in recent years, from 310 ppmv in 1958 to 370 ppmv in 2001 [Berger, 2002]. Researchers have predicted that a doubling of the atmospheric CO$_2$ concentration could increase global temperature by 1° to 5°C by the middle of this century [Rubin, et. al., 1992].

Prior to the industrial revolution, the relatively constant concentration of CO$_2$ in the atmosphere implied that the amounts of CO$_2$ generated by natural processes are almost equal to the amount absorbed by natural processes. However, human activity, mainly burning fossil fuels, produces about 24 billion tons of CO$_2$ per year and only half of that is being absorbed by natural processes [Morrissey and Justus, 1997].

1.2 Efforts to Reduce GHG Emissions

Research on reducing GHG emissions, including developing non-carbon energy sources, improving energy efficiency, and CO$_2$ capture and sequestration, has increased in recent years. In 1991, the International Energy Agency (IEA), funded by a consortium of governmental and industrial organizations, established a Greenhouse Gas Research and Development Programme [Matthews, 1996]. In 1990, the Japanese Ministry for International Trade and Industry (MITI) established the Research Institute of Innovative Technology for the Earth (RITE) through the New Energy Development Organization (NEDO). RITE has labs for global systems analysis and chemical CO$_2$ fixation and catalysis, and spends $140 million for biological CO$_2$ fixation and utilization and $70
million for CO₂ fixation in desert areas using biological function (developing plants to
green the deserts by means such as improving catalytic functions of microbial CO₂-fixing
enzymes) [Matthews, 1996]. The US Electric Power Research Institute (EPRI), funded by
power and fossil fuel companies from all corners of the world, was founded in 1973 and
they now support research on CO₂ capture and disposal [Matthews, 1996]. In 2001, the
Department of Energy (DOE) committed almost $25 million to co-fund eight new
exploratory projects to study methods to capture and store CO₂ [US DOE, 2001]. BP,
Chevron, ENI, Norsk Hydro, PanCanadian, Shell, Statoil, Suncor, and Texaco have
formed the CO₂ Capture Project (CCP) to develop technologies to reduce GHG emissions
[Hill and Moore, 2001].

Improving energy efficiency and using non-carbon energy sources are the most
effective in the short term (next 20 years) to reduce GHG emissions. Four important areas
are involved: improvement of thermo-electric energy conversion efficiency of power
generation plants, using technology such as natural gas combined cycle systems (NGCC);
better fuel efficiency in transportation, particularly automobiles, such as the introduction
of hybrid cars, fuel cell vehicles (FCV), and electric vehicles; more efficient heating and
hot water supplies in buildings and houses; and development of small scale power
sources like fuel cells [Kaya, 2002].

Over time, these methods may be effective in reducing CO₂ emissions, but
generally they are not applicable to the large number of existing fossil fuel fired power
plants. Therefore, CO₂ capture and sequestration to reduce the CO₂ concentration in the
atmosphere are needed during the next several decades. Theoretically we can remove
CO₂ from the air by enhancing natural sinks, such as growing more algae by ocean
fertilization, planting trees, and greening the desert [Matthews, 1996]. These ideas have long-term significance, but are not practicable at present; therefore CO$_2$ capture from fossil fuel fired emission sources must receive the current research emphasis.

### 1.3 CO$_2$ Capture and Sequestration

Since fossil fuels account for 90 percent of global energy consumption currently and cannot be phased out rapidly, we must rely on fossil fuels as the main energy source for the next several decades [Greenhouse Issues, 1997]. Thus carbon capture and sequestration to reduce the release of CO$_2$ to atmosphere from stationary sources like fossil fuel fired power plants is of critical importance.

The idea behind carbon sequestration is to find large reservoirs for storing CO$_2$ rather than allowing it to discharge to the atmosphere. After separating and compressing CO$_2$ from combustion stack gases, liquid CO$_2$ can be transported and discharged into the bottom of the ocean, stored in geological formations, stored in the form of dry ice, or fixed by *in situ* lakes of algae [Matthews, 1996], or converted to benign solid materials or fuels through biological or chemical processes [Beecy, *et. al.*, 2001].

Most current emphasis is placed on geologic sequestration (GEO-SEQ). There are numerous natural sinks for CO$_2$—depleted oil and gas fields, deep unminable coal seams, rich gas bearing shales, and deep saline formations [Beecy, *et. al.*, 2001]. In addition, the captured CO$_2$ can be an effective solvent to improve oil recovery in Enhanced Oil Recovery (EOR) and used to increase the production of methane from coal beds (ECBM) [Hill and Moore, 2001].
The first step, separation and compression (i.e. capture), is currently considerably more costly than transportation and sequestration. Thus, developing new technology to reduce capture costs is the principal research topic at present.

The various CO$_2$ capture options include adsorption of the gas using molecular sieves, physical and chemical absorption by solvents, low temperature (cryogenic) separation processes, and use of membranes [Capture and Storage of CO$_2$, 2002]. Although various processes for CO$_2$ capture are under development, only liquid amine-based absorption systems are used commercially now [RTI, 2000]. Because conventional amines are degraded and lose capacity due to the typical contaminants (e.g. O$_2$, SO$_2$, HCl, and particulates) found in flue gas, as well as high capital and operating costs associated with CO$_2$ separation from large volumes of flue gas at low CO$_2$ concentrations, the commercial amine-based capture processes for separating CO$_2$ from flue gas have not been widely adopted [RTI, 2000].

1.4 Project in this Thesis

The purpose of this research is to develop a simple, inexpensive technology to remove CO$_2$ as an essentially pure stream from flue gas using a regenerable sodium bicarbonate-based sorbent. The sorbent is regenerated to produce CO$_2$ and H$_2$O. After condensing the H$_2$O, a pure CO$_2$ stream is produced for subsequent use or sequestration. The relevant reaction based upon the use of sodium bicarbonate as the sorbent precursor is as follows:

$$2\text{NaHCO}_3 (s) \leftrightarrow \text{Na}_2\text{CO}_3 (s) + \text{CO}_2 (g) + \text{H}_2\text{O} (g)$$

The forward step is used for sorbent regeneration and CO$_2$ release, while the reverse reaction is used for CO$_2$ removal.
Additionally, the process should be readily retrofitted to existing facilities and easily integrated with new power generation facilities.

In this research, an electrobalance and fixed-bed reactor are used to evaluate CO$_2$ capture from simulated flue gas using candidate Na-based sorbents. Preliminary information on sorbent durability is provided by multicycle tests. The effect of reaction parameters, including carbonation temperature, carbonation gas composition, and calcination temperature and atmosphere, are studied using a number of candidate sorbents. In addition, the effects of typical contaminants, such as O$_2$ and SO$_2$, on the activities and durability of the sorbents are studied.
2.1 CO₂ Capture Technologies

Various available technologies to separate and capture CO₂ can be classified as follows:

- Physical and chemical absorption. For CO₂ concentrations such as found in the flue gas, a chemical solvent such as monoethanolamine (MEA) [Capture and Storage of CO₂, 2002] or a solid sorbent such as solid phase amine, silver oxide, or lithium hydroxide [Atwater, 1996] is preferred; for higher CO₂ concentration, e.g. CO₂ rejection from natural gas [Chakravarti et.al., 2001], a physical solvent is favored [Capture and Storage of CO₂, 2002].

- Physical and chemical adsorption by using a high surface area adsorbent, such as zeolite, alumina or activated carbon [Rao and Rubin, 2002].

- Low temperature (cryogenic) distillation by liquefaction and purification of CO₂ from high concentration (>90%) of CO₂ sources [Chakravarti et. al., 2001].

- Gas separation membranes using solubility-selective polymers for low-temperature separation and ceramics for high-temperature separation [DOE, 1999].

- Advanced processes such as CO₂ capture by an ionic liquids [Bates et. al., 2002], and a high pressure CO₂ separation process in an IGCC plant [Deppe, et. al., 2002].
The choice of CO$_2$ capture system depends on the power plant fuels and technologies. Figure 2.1 shows the variety of power generation technologies [Rao and Rubin, 2002].

Figure 2.1. Technology Options for Fossil Fuel Based Power Generation [Rao and Rubin, 2002].

Physical and chemical absorption separates CO$_2$ from a mixed gas by contacting the gas at low temperature with a liquid absorbent that can selectively absorb CO$_2$, and then heating the resultant solution to release the CO$_2$ out of the solution [Suzuki et al., 1997].

Physical and chemical adsorption accomplishes CO$_2$ separation by contacting a mixed gas with an adsorbent such as activated carbon or a molecular sieve containing micropores to selectively adsorb CO$_2$, and then separating the adsorbed CO$_2$ via changing pressure or temperature, i.e., pressure swing adsorption (PSA) or temperature swing adsorption (TSA). PSA involves the phases of increasing pressure, adsorption, rinsing, and reducing the pressure. TSA accomplishes adsorption at room temperature or lower,
and then elevates the temperature to release the CO$_2$ adsorbed [Suzuki, et al., 1997]. Normally PSA is preferable to TSA because regeneration can be accomplished faster. The preferred concentration of CO$_2$ in the flue gas for most effective CO$_2$ removal by adsorption is between 400ppm and 15000ppm. CO$_2$ concentration lower than 400ppm will result in limited capacity and poor selectivity [Capture and Storage of CO$_2$, 2002].

The disadvantage of PSA is the energy needed to increase the pressure, the cost of the equipment for adsorption, and the fact that most adsorbents are highly expensive [Suzuki, et al., 1997]. Disadvantages of TSA include the large energy cost to produce steam for adsorbent regeneration, the large time required to switch between high temperature and room temperature, and the need for a large heating device [Suzuki, et al., 1997]. Neither can be easily utilized to recover specific gaseous components from low-grade waste gas because of the high cost.

Molecular sieves are used to remove CO$_2$ by adsorption (physisorption) in the space station, but their high cost limits their usage for CO$_2$ capture form flue gas [Atwater, 1996].

Cryogenic processes can produce liquid CO$_2$ ready for transportation prior to use or sequestration, but is only worth considering when the CO$_2$ concentration in flue gas is high [Capture and Storage of CO$_2$, 2002] (>90% CO$_2$) [Chakravarti, 2001].

2.1.1 Amine-Based Absorption Processes

2.1.1.1 Existing Amine-Based Technology

Historically, separating CO$_2$ from flue gas started in the 1970s, not because of concern about the greenhouse effect, but as a potentially economic source of CO$_2$, mainly for enhanced oil recovery (EOR) operations. In the late 1970s and early 1980s, several
commercial CO₂ capture plants were constructed in the U.S. Then in September 1996, the first commercial CO₂ absorption facility for CO₂ sequestration started in Norway. All these plants capture CO₂ with processes based on chemical absorption using a monoethanolamine (MEA)-based solvent. This technology can capture about 75-90% of the CO₂ and get a nearly pure (>99%) CO₂ product stream [Rao and Rubin, 2002].

To date, chemical absorption with amine is the only technique that has been used commercially to capture CO₂ from flue gas. Currently there are three electric power generating stations in the U.S. that capture CO₂ from flue gas and six other major flue gas CO₂ capture facilities worldwide. All nine use MEA as the chemical sorbent [Strazisar, et. al., 2001].

The general method involves exposing a gas stream to an aqueous amine solution that reacts with the CO₂ in the gas by an acid-base neutralization reaction to form a soluble carbonate salt:

\[ 2RNH_2 + CO_2 + H_2O \leftrightarrow (RHN_3)_2CO_3 \]

This reaction is reversible, so the CO₂ gas can be released by heating in a separate stripping column. Other amines such as diethanolamine (DEA), methyldiethanolamine (MDEA), or diisopropanolamine (DIPA) may also be used [Strazisar, et. al., 2001].

Figure 2.2 describes the operation of a typical amine based absorption plant for recovery of CO₂ from flue gas. The cooled and pretreated flue gas with tolerable levels of impurities such as SOₓ, NOₓ and particulates goes through a feed blower to overcome the pressure drop in the absorber, then passes into the absorption column with the temperature range of 40 to 45°C at the top and 50 to 60°C at the bottom. The flue gas and lean amine solution contact each other countercurrently in the absorber to selectively
Figure 2.2. Typical Amine Absorption Process for CO₂ Recovery from Flue Gas [Chakravarti, et. al., 2001].

absorb CO₂ from the flue gas by chemically reacting with the amine. Small amounts of oxygen physically dissolve in the amine solution. The CO₂-rich amine solution from the bottom of the absorber is pumped to the lean/rich heat exchanger and heated to about 105°C by the lean amine solution. The heated CO₂-rich amine then enters the upper portion of the stripper with operating temperature of 110°C at the top and 120°C at the bottom. Operating pressure at the bottom of the stripper and in the reboiler is around 30 psia and the pressure drop across the column is about 3 psia. Saturated stream at a pressure of 45 psia or higher provides the energy for stripping by heating the amine solution in the reboiler. Some water in the amine solution enters the stripper as stream and helps desorb CO₂ from the rich amine solution. Most of the lean amine solution is pumped to the lean/rich heat exchanger and a small portion of it is fed to a reclaimer for the removal of any degradation byproducts and heat-stable amine salts by the addition of
soda ash or caustic soda. The CO$_2$-rich vapor stream from the top of the stripper is partially condensed through a reflux condenser. The CO$_2$ product stream at a pressure of about 25 psia is dried and compressed to a high pressure required for sequestration. [Chakravarti, 2001].

Chemical absorption with amines is the most cost-effective means of directly obtaining high purity (>99%) CO$_2$ from flue gases in one step [Chakravarti, et. al., 2001]. Since this technology is effective for dilute CO$_2$ streams, commercially available and in use today, and similar to other end-of-pipe environmental control systems used at power plants, it is most suitable for combustion-based power plants [Rao and Rubin, 2002].

The adoption of amine-based processes for CO$_2$ capture is extremely slow. One reason is the high cost associated with CO$_2$ separation from flue gas at a very low CO$_2$ partial pressure. Another is that the presence of contaminants such as O$_2$, SO$_2$, NO$_X$, HCl, hydrocarbons, particles, and Hg in the flue gas reduces the absorption capacity of amines significantly, degrades the conventional amines rapidly, and results in operational problems such as foaming and corrosion [DOE, 1999].

Alternate solvents that eliminate or minimize the problems associated with amines are under development. An improved solvent should have higher CO$_2$ absorption capacity, faster CO$_2$ absorption rate, low vapor pressure, high degradation resistance, and low corrosivity. A number of energy efficient proprietary solvents have been studied based on either sterically hindered amines or formulated amines. The PSR solvent is a proprietary solvent [Veawab et. al., 2001] that can be formulated to provide optimized separation of CO$_2$ from any gas streams. One of the advantages of the PSR solvent is its flexibility, i.e., its various ingredients enable it to be optimized to meet the needs of
specific tasks. The key features of the PSR solvents are lower solvent circulation rate, lower regeneration temperature, lower solvent degradation rate and lower corrosion rate [Veawab *et al.*, 2001].

### 2.1.1.2 Praxair’s Advanced Amine Technology [Chakravarti, *et al.*, 2001]

Oxygen in the flue gas causes rapid degradation of alkanolamine which results in corrosion and significant deterioration by degradation byproducts. Praxair’s Advanced Amine Technology, including an oxygen tolerant amine absorption process and the application of amine blends, has been developed to overcome the low partial pressure of CO$_2$ and the presence of oxygen. The key aspect of Praxair’s approach is to handle the dissolved oxygen in the amine solution through process modifications instead of the introduction of additional chemicals. The CO$_2$-rich amine is heated to a temperature between 60°C to 90°C and then deoxygenated by depressurization.

Figure 2.3 depicts a process flow diagram for Praxair’s improved absorption process. The CO$_2$-rich amine is passed from the first lean/rich heat exchanger to a flash tank and its pressure is reduced from slightly above atmospheric pressure to subatmospheric pressure by using a vacuum pump. Oxygen and some CO$_2$ are released by depressurization. This O$_2$-rich stream can be directly mixed with CO$_2$-rich stream from the stripper for subsequent compression. The resulting oxygen depleted CO$_2$-rich amine solution typically contains less than 0.5 ppm oxygen. It is withdrawn from the flash tank and passed through a second heat exchanger to be further heated to around 105°C. This process avoids the need for inhibitors to slow down the oxidation degradation of the alkanolamines since the amine solution is heated after most of the oxygen has been removed.
Figure 2.3. Improved Absorption Process with Vacuum Flash [Chakravarti, et. al., 2001].

Another method for deoxygenation is stripping the dissolved oxygen from the CO₂-rich amine in a stripping column by means of an oxygen scavenging gas such as nitrogen or the CO₂-vapor product from the CO₂ capture process.

The MEA-based system requires energy to heat the solution and release CO₂. Higher MEA concentrations will reduce the energy consumed in heating extra water, but corrosion becomes significant at concentrations above 30 wt.%. Other amines such as MDEA have the potential of greater capacity and reaction rates without corrosion problems. The concentration of Praxair’s amine blends, containing 10-20 wt.% MEA and 20-40 wt.% MDEA, can reach 50 wt.%.
2.1.1.3 Rate Promoter – Piperazine (PZ) [Dang and Rochelle, 2001]

MEA reacts relatively fast with CO$_2$, but the absorption rate is still affected by reaction kinetics. Typical absorber tray efficiency is less than 20%. The rate constant of a PZ/MEA solution with CO$_2$ is one order of magnitude higher than that of MEA with CO$_2$, so a blend of MEA and PZ (MEA/PZ/water) should absorb CO$_2$ faster than MEA alone. The absorption rate of CO$_2$ at 40$^\circ$C and 60$^\circ$C in aqueous MEA with 0.6 to 1.2 M PZ is 1.5-2.5 times greater than in MEA alone. The PZ species contributes more than 60% of the total absorption rate with less than 0.4 mol CO$_2$ / mol amine, and accounts for more than 40% of the total absorption rate with more than 0.6 mol CO$_2$/mol amine. At 40 and 60$^\circ$C and loading greater than 0.4 to 0.5 mol CO$_2$ / mol amine, the equilibrium partial pressure of CO$_2$ in aqueous MEA/PZ with 0.6 to 1.2 M PZ is 2 to 5 times smaller than MEA alone. At loading less than 0.2 to 0.3, PZ has no significant effect on the equilibrium partial pressure of CO$_2$.

2.1.1.4 Vortex Contactor [Raterman, et. al., 2001]

Diffusion is another factor that affects the rate of absorption of CO$_2$ by aqueous alkanolamine solution. The two-film theory of gas-liquid absorption states that CO$_2$ transfer from the bulk gas to the liquid phase is mediated by diffusion through stagnant gas and liquid films about the interface. Increasing the turbulent mixing between gas and liquid can reduce the resistance to mass transfer in these films. Likewise, increasing the interfacial area to mass transfer per unit volume can enhance the absorption rate. Thus an improved contactor design should promote higher transfer kinetics by creating turbulence and a greater interfacial area for mass transfer.
Shear jet absorbers exhibit the highest mass transfer fluxes among the various contactor designs used at present, but the high mass transfer efficiencies are attained at the expense of energy. A vortex tube contactor is designed to achieve high mass transfer efficiencies while minimizing energy requirement. The separation is performed by forcing an expanding gas and dispersed liquid absorbent into a turbulent rotational flow field in order to facilitate CO₂ transfer. Then the subsequent liquid separation from CO₂-free gas is performed in the same device fitted with a liquid collector. This separation is analogous to centrifugal or cyclonic separation. The clean gas is discharged for end use while the liquid absorbent is regenerated and recycled. After regeneration, the relatively pure CO₂ may be captured for sequestration. This process is said to significantly reduce absorbent fluxes and thus reduces both capital and operation expenses. In this process, the cost of gas compression can be minimized with a variable aperture nozzle design. The vortex tube contactor may be broadly applied to natural gas upgrading and greenhouse gas capture from large to small point sources.

2.1.2 Ammonia

2.1.2.1 Anion-Exchange Resin for Ammonia Regeneration [Huang et. al., 2002]

Although the processes based on chemical absorption with monoethanolamine (MEA) or diethanolamine (DEA) are the most widely used technology for the capture of CO₂ from flue gas, they are still too expensive in the absence of regulations requiring CO₂ capture for large-scale applications such as the sequestration of CO₂ from power plants. The ammonia scrubbing technology possesses many advantages over the conventional MEA process for CO₂ capture, including lower cost, higher capacity and efficiency for CO₂ absorption, lower decomposition temperature of ammonium
bicarbonate, and less corrosion to absorber material. However, in addition to the highly volatile nature of ammonia, the lack of a process to regenerate ammonia from its carbonate salts hinders the ammonia scrubbing technique from being applied in practice.

An anion-exchange resin with a free amine functional group can absorb \( \text{H}_2\text{CO}_3 \) from a \( \text{NH}_4\text{HCO}_3 \) solution to release the ammonia; the ammonia then combines with the remaining \( \text{NH}_4\text{HCO}_3 \) to form ammonium carbonate at room temperature:

\[
\text{R-NH}_2 \rightleftharpoons \text{R-NH}_2 \cdot \text{H}_2\text{CO}_3 + \text{NH}_3
\]

\[
\text{NH}_3 + \text{NH}_4\text{HCO}_3 \rightleftharpoons (\text{NH}_4)_2\text{CO}_3
\]

The regenerated ammonium solution should contain ammonia and ammonium carbonate, and both ammonia and ammonium carbonate can absorb \( \text{CO}_2 \):

\[
\text{CO}_2 + \text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4\text{HCO}_3
\]

\[
\text{CO}_2 + (\text{NH}_4)_2\text{CO}_3 + \text{H}_2\text{O} \rightleftharpoons 2\text{NH}_4\text{HCO}_3
\]

The ammonium carbonate concentration in the absorbent significantly impacts the volatility of ammonia and \( \text{CO}_2 \) removal efficiency. Taking account of both the volatility of the ammonia and the energy consumption, a reasonable total ammonium carbonate solution concentration is 0.25 M. At this concentration, when \( \text{pH} = 9.0 \), the ammonia equilibrium vapor pressure is 0.0031 atm and the \( \text{CO}_2 \) removal efficiency can reach 86.1%; with \( \text{pH} = 11.0 \), the ammonia equilibrium vapor pressure is 0.0086 atm and the \( \text{CO}_2 \) removal efficiency can achieve 100%.

The resin can be regenerated by hot water at temperatures of 50°C or higher to liberate \( \text{CO}_2 \):

\[
\text{R-NH}_2 \cdot \text{H}_2\text{CO}_3 \rightleftharpoons \text{R-NH}_2 + \text{CO}_2 + \text{H}_2\text{O}
\]
The regeneration capability of the recycled resin can be repeatedly kept at 87% of that of the original resin. The energy required is reported to be approximately 50% less than that for the MEA process.

2.1.3 Membranes

Membrane separation operates by passing the mixed gas over a CO$_2$ selective membrane having different pressure on either side of the membrane [Suzuki, et al., 1997]. One attractive property of membranes is that they require less energy for operation than other CO$_2$ capture methods [Capture and Storage of CO$_2$, 2002]. The principle of a membrane contactor for gas absorption is shown in Figure 2.4. The essential element is a porous, water repellent, polymeric membrane. The gas containing CO$_2$ is fed along one side of the membrane. CO$_2$ diffuses through the gas filled pores of the membrane and is then absorbed into the absorption liquid on the other side [Feron, 2002].

![Figure 2.4. Membrane Gas Absorption Principle [Feron, 2002]](image)

Membrane contactors have many potential advantages over conventional scrubbers for gas sorption, such as large contact areas per unit volume (as much as 300 to
1000 M⁻¹), no flooding and foaming phenomena, high removal efficiency, larger treatment capacity, low energy consumption and easy scale-up [Xu, et. al., 2001].

A suitable combination of absorption liquid and membrane is key for this process. The membrane material must allow the pores to remain gas-filled at an excess pressure more than 1 bar on the liquid side so that the liquid will not leak through the membrane [Feron., 2002].

Even though membranes have been used commercially in hydrogen separation [Capture and Storage of CO₂, 2002], the utilization of membranes to separate CO₂ from the flue gas is limited by the low selectivity and low membrane permeability. Research on CO₂ capture using membranes emphasizes both improving selectivity and permeability. In general polymer membranes do not exhibit both high permeability and high selectivity; increasing permeability will cause loss in selectivity and vice versa [Xu, et. al., 2001].

In recent years, a variety of nanostructured materials have been investigated to solve the conflict between permeability and selectivity. Novel PMDA-ODA polyimide / polystyrene nanocomposite membranes have proved to possess both high gas permeability and high selectivity [Xu, et. al., 2001].

Similarly, a polypropylene hollow fiber membrane (PPHFM) contactor, with aqueous solution absorbent such as sodium hydroxide (NaOH), monoethanolamine (MEA) and diethanolamine (DEA), has been reported to give with both high permeability and high selectivity [Xu, et. al., 2001].

Gas separation using ceramic membranes is also being studied. Ceramic composite membranes have higher thermal and chemical stability and improved
regenerability compared to polymeric membranes. In order to enhance the CO\textsubscript{2}/N\textsubscript{2} separation factor gas transport mechanisms such as molecular sieving, activated diffusion, and surface diffusion instead of Knudsen diffusion are important. Ceramic membranes having pore sizes less than 10 Å and surface modifications are important. Research has been conducted on zeolite membranes because their very small and uniform pore structures and their strong hydrophobicity can prevent loss of gas permeability due to moisture adsorption. The ZSM-5 zeolite membrane has proved to be effective for CO\textsubscript{2} separation. In recent years, organic template-derived amorphous/nanoporous silica composite membranes with uniform pore sizes, which are expected to exhibit molecular sieving behavior and high permeability, have been getting more attention [Yang, et. al., 2002].

2.1.4 CO\textsubscript{2} Capture by a Task-Specific Ionic Liquid (TSIL) [Bates, et. al., 2002]

When capturing CO\textsubscript{2} by a liquid absorption, the vapor pressure of the solvent will cause some loss of the solvent into the gas stream. Ionic liquids (low-temperature molten salts) have been proposed to avoid the problem. The Coulombic attraction between the ions of these liquids results in the absence of measurable vapor pressure up to their decomposition point (>300°C). These materials without vapor pressure may be thought as “liquid solids”, and incorporate some of the useful physical properties of both phases. A solvent called TSIL is an example of this kind of material. The cation of the TSIL consists of an imidazolium ion to which a primary amine moiety is covalently tethered. The new ionic liquid is prepared from commercially available starting materials. The cation core is assembled by the reaction of 1-butylimidazole with 2-bromopropylamine hydrobromide in ethanol. The product imidazolium bromide is a relatively viscous,
water-free liquid, which can react reversibly with CO₂, and be repeatedly recycled. The proposed reaction between TSIL 1 and CO₂ is given below:

\[
2 \text{TSIL} + \text{CO}_2 \rightarrow \text{Product}
\]

Compared with the commercial amine sequestering reagents, TSIL has higher efficiency for CO₂ capture.

### 2.2 Technology Investigated in this Thesis

Chemical adsorption of CO₂ with a regenerable solid sorbent (dry scrubbing) is also a potential technique for CO₂ capture. Sorbents containing alkali- and alkaline-earth metals like potassium carbonate and calcium oxide are investigated for their commercial feasibility [Hoffman and Pennline, 2001]. In addition, the amine-enriched sorbents, which can be prepared by the chemical treatment of the surface oxide material with various amine compounds, have the potential of capturing/releasing CO₂ [Soong, et. al., 2001].

The high cost of separating CO₂ from flue gases is a major barrier to wider use of CO₂ removal technology. Therefore, a relatively inexpensive process for CO₂ capture from flue gas is needed to make reduction of CO₂ emissions an economically viable global goal. The objective of this research is to study a simple, inexpensive CO₂ separation process using a dry, regenerable sodium-based sorbent that may be applicable
to existing fossil fuel combustion sources. With possible application to all conventional steam-generating power plants, the proposed technology has the potential to capture more than 440 million metric tons of carbon equivalent per year [RTI, 2000].

Figure 2.5 shows the integration of the proposed regenerable sodium bicarbonate-based sorbent technology into a fossil fuel fired power plant with the final products being a stack gas essentially free of CO$_2$ and a pure CO$_2$ gas stream suitable for commercial sale or sequestration. Sodium bicarbonate (NaHCO$_3$) is used as the basis for the dry, regenerable sorbent technology, and the primary reactions in this process are given below:

CO$_2$ capture (Carbonation)

$$\text{Na}_2\text{CO}_3 (s) + \text{CO}_2 (g) + \text{H}_2\text{O} (g) = 2\text{NaHCO}_3 (s)$$

CO$_2$ release (Decarbonation / Calcination)

$$2\text{NaHCO}_3 (s) = \text{Na}_2\text{CO}_3 (s) + \text{CO}_2 (g) + \text{H}_2\text{O} (g)$$

![Figure 2.5. Integration of the Proposed Process in a Generic Fossil Fuel Combustion Facility [RTI, 2000]]
When the flue gas from the fossil fuel combustion facility flows into the carbonation reactor, CO$_2$ is absorbed by the sorbent and the CO$_2$-free product gas is sent to the stack for exhaust. The sorbent is transported to the decarbonation reactor where regeneration releases CO$_2$ and H$_2$O. The regenerated sorbent is transferred back to the carbonation reactor. The released CO$_2$ and water vapor flow into the water condenser. The condensed water is removed and a near pure CO$_2$ (> 99%) stream is obtained for sequestration.

In addition to the primary product, sodium bicarbonate, by-products including Na$_2$CO$_3$$\cdot$H$_2$O, Na$_2$CO$_3$$\cdot$NaHCO$_3$$\cdot$2H$_2$O, and Na$_2$CO$_3$$\cdot$3NaHCO$_3$ (Wegscheider’s salt) can be formed at carbonation conditions studied in this research. The possible existence of contaminants in the flue gas, such as HCl, SO$_2$ and O$_2$, can result in the deactivation of sodium bicarbonate by the formation of stable products like NaCl, Na$_2$SO$_3$ and Na$_2$SO$_4$. The thermodynamic analysis of these reactions will be discussed in Chapter 3.
Chapter 3
Thermodynamic Analysis

This chapter focuses on the thermodynamic analysis based on results from HSC Chemistry [Roine, 1997] and phase diagrams. Calcination and carbonation temperatures, calcination atmosphere, gas composition, and possible products are discussed thermodynamically.

3.1 HSC Chemistry

The thermodynamics associated with the primary reaction, by-product reactions and reactions involving potential flue gas contaminants have been analyzed using HSC Chemistry 4.1 [Roine, 1997], a chemical reaction and equilibrium software. HSC 4.1 contains a database that includes thermochemical data for more than 15000 compounds. It is used to calculate thermochemical equilibrium based on the free energy minimization approach.

When using HSC, the initial composition of the reactants, possible products at equilibrium, phase of each compound (gas, liquid or solid), temperature, and pressure of the system must be specified. Calculation can be based on stepwise intervals of the amount of a single initial component, reaction temperature, or pressure. The equilibrium composition or mole amounts are presented as a function of the amount of a desired compound, temperature, or pressure.

HSC does not take into account the kinetics of the chemical reactions. Also all the reactions are calculated based on a batch system. Thus HSC provides only an approximation of the actual system. However, the use of HSC permits rapid screening to identify appropriate ranges of reaction conditions to be studied experimentally, hence minimizing expensive trial-and-error chemistry.
3.2 Possible By-Products and Contaminants

Besides the primary product NaHCO₃, the possible formation of by-products including Na₂CO₃•H₂O, Na₂CO₃•NaHCO₃•2H₂O, and Na₂CO₃•3NaHCO₃ (Wegscheider’s salt) at carbonation condition has been examined using HSC. The relevant reactions are as follows:

\[
\begin{align*}
Na₂CO₃ (s) + CO₂ (g) + H₂O (g) & \leftrightarrow 2NaHCO₃ (s) \\
Na₂CO₃ (s) + H₂O (g) & \leftrightarrow Na₂CO₃•H₂O (s) \\
Na₂CO₃ (s) + 1/3CO₂ (g) + 5/3H₂O (g) & \leftrightarrow 2/3Na₂CO₃•NaHCO₃•2H₂O (s) \\
Na₂CO₃ (s) + 3/5CO₂ (g) + 3/5H₂O (g) & \leftrightarrow 2/5Na₂CO₃•3NaHCO₃ (s)
\end{align*}
\]

(Wegscheider’s salt)

All of these reactions are reversible at calcination conditions of interest. With the exception of reaction (3.2), all result in CO₂ removal, but the efficiency of reactions (3.3) and (3.4) is less than the efficiency of reaction (3.1). Hence, reaction (3.1) is the desired reaction.

HCl and SO₂ in the flue gas may also react with Na₂CO₃ according to the following reactions:

\[
\begin{align*}
Na₂CO₃ (s) + 2HCl (g) & \rightarrow 2NaCl (s) + CO₂ (g) + H₂O (g) \\
Na₂CO₃ (s) + SO₂ (g) & \rightarrow Na₂SO₃ (s) + CO₂ (g) \\
Na₂CO₃ (s) + SO₂ (g) + 0.5O₂ (g) & \rightarrow Na₂SO₄ (s) + CO₂ (g)
\end{align*}
\]

However, these reactions involving HCl and SO₂ are not reversible under calcination conditions of interest, and will result in the cumulative deactivation of the sorbent.
3.3 Equilibrium Constant

The equilibrium constant of a given reaction is defined by

\[ K = \exp \left( -\frac{\Delta G^0}{RT} \right) = \prod a_i^{\nu_i} \]

where: 
- \( K \) – equilibrium constant
- \( \Delta G^0 \) – standard Gibbs energy of a reaction
- \( R \) – gas constant, = 1.987 cal/(K\text{ mol}) = 8.314 J/(K\text{ mol})
- \( T \) – temperature in K
- \( a_i \) – activity of component \( i \)
- \( \nu_i \) – stoichiometric coefficient of component \( i \) (positive for products and negative for reactants)

Large values of \( K \) indicate that the reaction is thermodynamically favored.

The equilibrium constants for reactions (3.1) through (3.7) are presented in Table 3.1. All reactions are exothermic as indicated by the fact that \( K \) decreases with increasing temperature. The carbonation and hydration reactions are favored only at the lower temperatures while the reactions involving contaminants are favored over the entire temperature range.

3.4 Equilibrium Compositions

In the following analysis all gas phase components were assumed to be ideal and all solids were assumed to form pure components. Thus

- Gas: \( a_i = y_i P \)
- Solid: \( a_i = 1 \)

where: \( y_i \) – mole fraction of gas component \( i \)

\( P \) – pressure in the system
Table 3.1 Equilibrium Constants for Possible Reactions in this System

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Log K for Reaction</th>
<th>Log K for Reaction</th>
<th>Log K for Reaction</th>
<th>Log K for Reaction</th>
<th>Log K for Reaction</th>
<th>Log K for Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>3.592</td>
<td>0.982</td>
<td>2.445</td>
<td>2.028</td>
<td>24.086</td>
<td>8.126</td>
</tr>
<tr>
<td>70</td>
<td>2.972</td>
<td>0.71</td>
<td>1.882</td>
<td>1.653</td>
<td>23.437</td>
<td>7.848</td>
</tr>
<tr>
<td>80</td>
<td>2.387</td>
<td>0.453</td>
<td>1.351</td>
<td>1.299</td>
<td>22.825</td>
<td>7.587</td>
</tr>
<tr>
<td>90</td>
<td>1.835</td>
<td>0.211</td>
<td>0.848</td>
<td>0.964</td>
<td>22.246</td>
<td>7.34</td>
</tr>
<tr>
<td>100</td>
<td>1.312</td>
<td>-0.019</td>
<td>0.373</td>
<td>0.647</td>
<td>21.698</td>
<td>7.106</td>
</tr>
<tr>
<td>120</td>
<td>0.345</td>
<td>-0.445</td>
<td>-0.508</td>
<td>0.058</td>
<td>20.686</td>
<td>6.674</td>
</tr>
<tr>
<td>140</td>
<td>-0.527</td>
<td>-0.832</td>
<td>-1.304</td>
<td>-0.476</td>
<td>19.772</td>
<td>6.284</td>
</tr>
<tr>
<td>160</td>
<td>-1.318</td>
<td>-1.184</td>
<td>-2.03</td>
<td>-0.964</td>
<td>18.941</td>
<td>5.929</td>
</tr>
<tr>
<td>180</td>
<td>-2.038</td>
<td>-1.508</td>
<td>-2.694</td>
<td>-1.411</td>
<td>18.184</td>
<td>5.605</td>
</tr>
<tr>
<td>200</td>
<td>-2.697</td>
<td>-1.806</td>
<td>-3.304</td>
<td>-1.824</td>
<td>17.489</td>
<td>5.307</td>
</tr>
</tbody>
</table>

With these restrictions the equilibrium composition for the primary reaction (3.1) can be determined from

$$K = \frac{1}{y_{CO_2}y_{H_2}P^2}$$

A similar approach can be used for the other reactions.

Figures 3.1, 3.2 and 3.3 represent the equilibrium compositions as a function of temperature for CO₂ capture (Figure 3.1) and release (Figures 3.2 and 3.3) at a pressure of 1 atm when only the primary reaction (3.1) is considered. The initial mixture
Figure 3.1 Thermodynamics from HSC Chemistry – CO₂ Capture by Na₂CO₃

Figure 3.2 Thermodynamics from HSC Chemistry – CO₂ Release from NaHCO₃ in He
Figure 3.3 Thermodynamics from HSC Chemistry – CO₂ Release from NaHCO₃ in CO₂

Composition for CO₂ capture is 8 kmol CO₂, 16 kmol H₂O, 76 kmol He and 20 kmol Na₂CO₃, and those for CO₂ release are 38 kmol He (or 30 mol CO₂) and 40 kmol NaHCO₃. This carbonation gas approximates the H₂O and CO₂ contents obtained in the flue gas when methane is burned in 10% excess air. He was substituted for N₂ and O₂ since He was used in the TGA experiments to enhance the sensitivity of the electrobalance. The amount of He in calcination is picked for convenience and the mole amount of NaHCO₃ is equal to twice of that of Na₂CO₃ used for Figure 3.1. The amount of CO₂ in calcination is a little bit less than that of He to approximate the experimental calcination condition.

According to Figure 3.1, essentially complete carbonation is possible at temperatures lower than about 50°C and NaHCO₃ cannot exist at temperatures higher
than 90°C. The equilibrium amount of NaHCO$_3$ decreases very quickly as the temperature reaches about 75°C.

Figure 3.2 shows that NaHCO$_3$ can be completely calcinated to Na$_2$CO$_3$ at temperatures greater than 105°C in an atmosphere of He. Complete calcination would be possible at lower temperature if the amount of He in the initial mixture was increased. For comparison, Figure 3.3 shows NaHCO$_3$ calcination in an atmosphere of CO$_2$. NaHCO$_3$ is more stable in CO$_2$ and a temperature of about 115°C would be required for complete calcination. Similarly, increasing the CO$_2$ amount will decrease the temperature needed for complete calcination. For a commercial process that produces pure CO$_2$ suitable for sequestration, calcination must occur in a pure or nearly pure CO$_2$ atmosphere, which is the reason for studying calcination in a CO$_2$ atmosphere. However, the temperature needed for complete calcination in CO$_2$ is about 10°C higher than that in He. Thus He minimizes the required calcination temperature, and therefore minimizes the exposure severity of the sorbent. In addition, calcination in an atmosphere of He proceeds more quickly than in CO$_2$ and He enhances the sensitivity of electrobalance, therefore He was used in most of calcination tests.

Figure 3.4 compares the equilibrium carbonation composition of the four combined reactions (3.1) through (3.4) at temperatures between 40°C and 100°C. The initial conditions were the same as those for Figure 3.1. Over this temperature range, NaHCO$_3$ is the most important carbonation product. However, small amounts of Na$_2$CO$_3$•H$_2$O can be formed when the temperature is lower than 60°C if there is excess H$_2$O. Other by-products, Na$_2$CO$_3$•3NaHCO$_3$ (Wegscheider’s salt) and Na$_2$CO$_3$•NaHCO$_3$•2H$_2$O, are not predicted from HSC at these conditions. There is no
Figure 3.4 Thermodynamics from HSC Chemistry – Possible Products in Carbonation

difference in Figures 3.1 and 3.4 at temperatures above 60°C where Na₂CO₃•H₂O cannot be formed.

Figure 3.5 shows the equilibrium percent CO₂ removal as a function of temperature based on the results of Figure 3.4. With an increase in temperature, the equilibrium extent of CO₂ removal decreases because the carbonation reaction is exothermic. When the gas stream is composed of 8%CO₂, 16%H₂O and 76%He, with carbonation at 70°C and 1 atmosphere, it is theoretically possible to remove about 89% of the CO₂ from the flue gas.

3.5 Phase Diagrams

Phase diagrams for the system composed of NaHCO₃, Na₂CO₃, Na₂CO₃•H₂O, Na₂CO₃•3NaHCO₃, Na₂CO₃•NaHCO₃•2H₂O, CO₂ and H₂O as a function of temperature
Figure 3.5 Thermodynamics from HSC Chemistry – Equilibrium CO₂ Removal

and relative humidity have been supplied by Church & Dwight [Bracilovic, 1977] and are presented as Figures 3.6 through 3.9.

The relative humidity (RH) of the gas used in the previous calculations varies from 34% at 80°C to 81% at 60°C, and at a temperature of 70°C the relative humidity is 52%. For a CO₂ partial pressure of 0.08 atm, the favored products at temperatures of 60, 70, and 80°C and the relative humidities of 20%, 40%, 60% and 80% based on the phase diagrams are listed in Table 3.2. It is clear that NaHCO₃ is favored at 60°C for all relative humidities, while Na₂CO₃•3NaHCO₃ is favored at 80°C for almost all the relative humidities of interest. At 70°C the formation of NaHCO₃ or Na₂CO₃•3NaHCO₃ depends on the relative humidity. Generally lower temperature and higher relative humidity are favorable to the formation of NaHCO₃.
Figure 3.6 Phase Diagram for Sodium Carbonate/Sodium Bicarbonate System, RH = 20% [Bracilovic, 1977].
Figure 3.7 Phase Diagram for Sodium Carbonate/Sodium Bicarbonate System, RH = 40% [Bracilovic, 1977].
Figure 3.8 Phase Diagram for Sodium Carbonate/Sodium Bicarbonate System, RH = 60% [Bracilovic, 1977].
Figure 3.9 Phase Diagram for Sodium Carbonate/Sodium Bicarbonate System, RH = 80% [Bracilovic, 1977].
Table 3.2 Possible Products Predicted from Phase Diagrams for CO₂ Partial Pressure of 0.08 atm

<table>
<thead>
<tr>
<th>RH</th>
<th>60°C</th>
<th>70°C</th>
<th>80°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>20%</td>
<td>NaHCO₃</td>
<td>Na₂CO₃•3NaHCO₃</td>
<td>Na₂CO₃•3NaHCO₃</td>
</tr>
<tr>
<td>40%</td>
<td>NaHCO₃</td>
<td>Na₂CO₃•3NaHCO₃/NaHCO₃</td>
<td>Na₂CO₃•3NaHCO₃</td>
</tr>
<tr>
<td>60%</td>
<td>NaHCO₃</td>
<td>NaHCO₃</td>
<td>Na₂CO₃•3NaHCO₃</td>
</tr>
<tr>
<td>80%</td>
<td>NaHCO₃</td>
<td>NaHCO₃</td>
<td>Na₂CO₃•3NaHCO₃/NaHCO₃</td>
</tr>
</tbody>
</table>

For CO₂ partial pressure of 0.08 atm and H₂O partial pressure of 0.16 atm, the relative humidity and the favored product at temperatures of interest are listed in Table 3.3. According to these phase diagrams, by-products such as Na₂CO₃•NaHCO₃•2H₂O and Na₂CO₃•H₂O will not be formed at the gas compositions and temperatures of interest.

Table 3.3 Possible Products Predicted from Phase Diagrams for CO₂ Partial Pressure of 0.08 atm and H₂O Partial Pressure of 0.16 atm

<table>
<thead>
<tr>
<th>Temperature</th>
<th>RH</th>
<th>Possible Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>60°C</td>
<td>81%</td>
<td>NaHCO₃</td>
</tr>
<tr>
<td>70°C</td>
<td>52%</td>
<td>NaHCO₃</td>
</tr>
<tr>
<td>80°C</td>
<td>34%</td>
<td>Na₂CO₃•3NaHCO₃</td>
</tr>
</tbody>
</table>

3.6 Conclusion

The phase diagrams and HSC predict the same stable product of NaHCO₃ at 60°C and 70°C for carbonation conditions of 8% CO₂, 16% H₂O and balance He, while different stable phases at 80°C are given: Na₂CO₃•3NaHCO₃ using phase diagrams and NaHCO₃ using HSC. Since the calculations of HSC were based on ideal assumptions
while phase diagrams are presumably based on experimental data, the phase diagrams should be more reliable. In the real reaction system, the product may be a mixture of $\text{Na}_2\text{CO}_3\cdot3\text{NaHCO}_3$ and $\text{NaHCO}_3$ at 80°C.
Chapter 4
Experimental Systems, Procedure and Materials

A thermogravimetric analyzer (electrobalance) and fixed-bed reactor were the primary tools used in this research to evaluate the capture of CO₂ from simulated flue gas using sodium-based regenerable sorbents. This chapter describes the reactors and experimental procedures, and describes the properties of the sodium-based sorbent materials.

4.1 Thermogravimetric Analyzer (TGA) System

A Cahn Instruments Inc. Model 2000 TGA was used to study the effects of reaction parameters such as temperature and gas composition on reaction rates and sorbent capacity. The TGA monitors the change in weight of a reacting solid as a function of time, and the data can be used to calculate reaction rate and fractional conversion of the solid reactant. The system includes a Cahn 2000 electrobalance, a MicRIcon temperature programmer/controller, a nichrome resistance furnace, and a gas flow system. Experimental temperature and solid weight were collected using Labtech Notebook V12 real-time data acquisition and stored on a laboratory PC.

The system has a temperature range up to 1000° C, a capacity of 1.0 gram, a sensitivity of 0.2 μg and an accuracy of ±0.1 percent. The balance operates on a null-balance principal using a high sensitive transducer coupled to a taut-band suspension system to detect minute changes in the mass of a sample. An optically actuated servo loop maintains the balance arm in the horizontal reference (null) position by regulating the amount of current flowing through the transducer coil. An infrared light emitting diode and a pair of photosensitive diodes detect movement of the beam. A flag at the top of the balance arm controls the amount of light reaching each photosensor. As sample
weight is lost or gained, the beam becomes unbalanced, causing the light to strike the
photodiodes unequally. The unbalance signal is fed into the control program, where it is
zeroed. This changes the amount of current supplied to the meter movement, causing the
balance to rotate back to its null (zero) position. The amount of current required is
directly proportional to the change in the mass of the sample.

At the same time, the temperature programmer/controller controls the temperature
at a specified isothermal value or according to a linear rate of temperature increase or
decrease with time. The weight and temperature are recorded simultaneously into a data
file by the data acquisition board and software.

Figure 4.1 shows the TGA system schematically. Inert gas (either N\textsubscript{2} or He) is
added directly into the balance mechanism through upper flow path to prevent corrosive
gases from contacting the electronic components. Reactive gases containing CO\textsubscript{2}, H\textsubscript{2}O,
and the remainder of the He or N\textsubscript{2} are fed through the side arm of the hang-down tube of
the quartz reactor. Combined gases flow downward past the reacting solid, exit from the
bottom of the reactor tube, and are vented through a laboratory hood. All gases except
water vapor are obtained from high-pressure, high-purity cylinders and flow rates are
controlled using needle valves and calibrated rotameters. H\textsubscript{2}O is fed as liquid using a
Harvard Apparatus Model 909 high-pressure positive displacement syringe pump with 50
ml capacity, and the feed lines are heat-traced and insulated from the outlet of the pump
to insure vaporization of water when it mixes with other feed gases. The bottom of the
quartz reactor tube is also heated and insulated to prevent condensation of water vapor.

The reacting solid is held in a nonreactive aluminum pan or quartz cup and
suspended from the electrobalance using a nichrome or platinum wire. Reaction
Figure 4.1 Schematic Diagram of the TGA System
temperature is monitored using a chromel-alumel thermocouple placed approximately 1/4 inch below the sample container. The thermocouple signal is transmitted to the MicRIcon temperature programmer/controller and the temperature is controlled using a nichrome resistance furnace. A temperature limit switch in the MicRIcon controller is used to shut down the furnace if overheating should occur.

4.2 Experimental Procedure with TGA

Base case reaction conditions are shown in Table 4.1. Results from experimental tests that examined the effect of carbonation and calcination temperature and gas composition were compared to results from these base case conditions. Base case carbonation gas composition was chosen to approximate the flue gas composition resulting from the combustion of natural gas (CH$_4$) using 10% excess air. Base case calcination conditions, while not practical in commercial operation, were selected to expose the solvent to minimum severity.

Table 4.1 Base Case Reaction Conditions

<table>
<thead>
<tr>
<th></th>
<th>Calcination</th>
<th>Carbonation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>120</td>
<td>70</td>
</tr>
<tr>
<td>Pressure (atm)</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Gas Composition (mol%)</td>
<td>100% He</td>
<td>8 mol% CO$_2$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>16 mol% H$_2$O</td>
</tr>
<tr>
<td></td>
<td></td>
<td>76 mol% He</td>
</tr>
<tr>
<td>Gas Flow Rate (sccm)</td>
<td></td>
<td>600</td>
</tr>
</tbody>
</table>

The following experimental procedure was used in base case tests. About 75 mg of sorbent were placed in the quartz sample container suspended from the electrobalance using a platinum hangdown wire. After connecting all the feed lines, He was fed and Snoop leak detector was used to check for leaks. The test began with calcination of
NaHCO\textsubscript{3} to Na\textsubscript{2}CO\textsubscript{3} in an atmosphere of pure He, followed by carbonation in an atmosphere of He, CO\textsubscript{2} and H\textsubscript{2}O. During calcination, the carbonation gas composition of 8 mol\% CO\textsubscript{2}, 16 mol\% H\textsubscript{2}O and balance He at 600 sccm flowed to the bypass in order to stabilize the flow rate before carbonation began. Both product gas and bypass gas were sent to the vent through a condenser. During calcination the reactor was heated at 5\degree C/min from 20\degree C to 100\degree C and then at 1\degree C/min from 100\degree C to the final temperature of 120\degree C. After calcination was complete (as indicated by constant weight), the temperature was then decreased to the carbonation temperature of 70\degree C at a rate of 2\degree C/min. The direction of the three-way valve was changed to introduce reactive gases into the side arm of the reactor. Carbonation lasted about 3 hours until the reaction rate approached zero.

Appropriate changes in procedure were made when carbonation and calcination temperatures and gas compositions were altered from the base case. Table 4.2 summarizes the ranges of reaction conditions studied.

**Table 4.2 Sorbent Reaction Conditions Used in This Research**

<table>
<thead>
<tr>
<th></th>
<th>Calcination</th>
<th>Carbonation</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Temperature (\degree C)</strong></td>
<td>100, 120, 140, 150, 160, 170, or 200</td>
<td>50, 60, 65, 70, or 80</td>
</tr>
<tr>
<td><strong>Pressure (atm)</strong></td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td><strong>Gas Composition (mol %)</strong></td>
<td>100% He or 100% CO\textsubscript{2} or CO\textsubscript{2}:H\textsubscript{2}O = 4.2 (M:M)</td>
<td>CO\textsubscript{2}: 0%, 5%, 8%, 10% H\textsubscript{2}O: 5%, 10%, 16% SO\textsubscript{2}: 0%, 0.4%, 0.2%, 0.1% O\textsubscript{2}: 0%, 1.7%, 2% Balance He</td>
</tr>
<tr>
<td><strong>Flow Rate (sccm)</strong></td>
<td></td>
<td>300, 600, 900</td>
</tr>
</tbody>
</table>
4.3 The Fixed-Bed Reactor System

A fixed-bed reactor was used to determine the CO$_2$ removal efficiency by comparing the CO$_2$ content of the feed and product gases. It is composed of a reactor, a gas flow system, an Applied Test Systems Series 3210 single zone split-tube furnace, and a Shimadzu Model GC-14A gas chromatograph (GC).

Figure 4.2 represents the schematic diagram of the fixed-bed reactor system. Permanent gases such as N$_2$ and CO$_2$ were obtained from high-purity gas cylinders with flow rates controlled using Porter Instruments Model 201 mass flow controllers. Liquid H$_2$O was fed using a syringe pump as shown or by bubbling mixed gases through a gas wash bottle containing H$_2$O at a controlled temperature. Feed lines and the line between the reactor and condenser were heated and insulated to insure complete vaporization.

All reactor components were of 316 stainless steel. Solid reactant (sorbent) was held inside a reactor insert and supported on a porous stainless disk. Combined feed gases entered near the bottom of the reactor, flowed upward in the annular space between the reactor vessel and insert where the gases were preheated, then flowed downward through the solid sample, and exited from the bottom of reactor vessel. Product gases passed through an ice bath condenser to remove steam. The dry product gas then flowed to the gas chromatograph for analysis.

The reactor was designed by Han [1995] and consists of two main parts: the reactor vessel and insert as shown in Figure 4.3. It has a capacity of about 30g solid. A porous stainless steel disc supported the packed bed and a thin layer of quartz wool was inserted between the porous disc and the sorbent packing to prevent small solid particles
BPR : Back-Pressure Regulator
PRV : Pressure Relief Valve
CV : Check Valve
MFC : Mass Flow Controller
D : Dryer
F : Filter

Figure 4.2 Schematic Diagram of the Fixed-Bed Reactor System
Figure 4.3 The Fixed-Bed Reactor [Han, 1995]
from going through the stainless disc. A layer of quartz wool was also placed above the sorbent.

The reactor temperature was controlled by an Applied Test System Series 3210 single zone split-tube furnace, which has a temperature controller Model 2010 and a CFE limit controller Model 2040. The temperature controller can program up to 8 ramp-and-soak steps and 254 cycles.

4.4 Product Gas Analysis

A Shimadzu G14A GC equipped with an automatic 10-port sampling valve, dual columns, methanizer, thermal conductivity (TCD), and flame ionization (FID) detectors was used to determine the CO$_2$ concentration in the product gas as a function of time. The carrier gas was UHP nitrogen. Gas products from the condenser flowed into a HayeSep-N column to trap trace amounts of moisture escaping the condenser. The dry gases were then separated in a Carboxen 1000 column while the HayeSep-N column was back flushed to vent.

The GC sampling is represented schematically in Figure 4.4 [Lopez Ortiz, 2000]. A Valco Instruments automatic 10-port pneumatic valve sampled gas product every 12 minutes. The valve has two positions, known as LOAD and INJECTION. In the load position, product gas flowed into the sample valve, through the sample loop, back in the sampling valve, and to vent. The sample loop consisted of 1/8” Teflon tubing with an internal volume of approximately 0.5 cm$^3$. Carrier gas CG1 flowed through the sample valve to the HayeSepN column to backflush H$_2$O trapped from the previous sample, back to the valve, and then to vent. Carrier gas CG2 flowed through the valve to the Carboxen 1000 column where CO$_2$ was separated and then to the TCD, methanizer, and FID.
Position A – Load

Position B – Injection

= Restrictor

Figure 4.4 GC Operation Method [Balasubramanian, 1998]
In the injection position the product gas flowed directly to vent. Product gas contained in the sample loop was picked up by CG1 and flowed into the HayeSepN column to trap trace quantities of moisture. The dry gas then flowed through the Carboxen column where the CO\textsubscript{2} was separated. The separated gas components flowed into the TCD, then to a Ni-catalyzed methanizer where CO\textsubscript{2} was converted to CH\textsubscript{4}, and to FID to be analyzed. The FID is more sensitive than the TCD, and was used to analyze CO\textsubscript{2} concentration. Excess UHP hydrogen was fed to the methanizer to ensure complete conversion of CO\textsubscript{2} to CH\textsubscript{4} and to maintain a stable flame in the FID. The ratio of methanizer air to hydrogen was at least 10:1. After the gas was eluted from the carboxen column, the sampling valve switched back to the load position and the HayeSepN column was back flushed with CG1 to remove traces of water.

Shimadzu Class-VP Version 4.2 software was used for data acquisition and to control the sampling valve for automatic operation. Operating conditions and valve timing were determined by trial-and-error. The sampling interval was 12 minutes since 6 minutes were needed for complete separation of all components and 6 minutes to back flush the HayeSepN column. Table 4.3 [Lopez Ortiz, 2000] shows the GC operating conditions.

The FID calibration relating the mol percent CO\textsubscript{2} and the peak area was determined when feeding a known composition of CO\textsubscript{2}. Figure 4.5 shows the calibration curve and regression equation. The system was recalibrated periodically.

4.5 Experimental Procedure with Fixed-Bed Reactor

About 25 grams of sorbent were added to the reactor insert, which was coupled to the vessel with two o-rings to seal the system. After connecting all the feed lines, N\textsubscript{2} was
Table 4.3 GC Calibration Standards [Lopez Ortiz, 2000]

<table>
<thead>
<tr>
<th>Carrier Gas</th>
<th>Nitrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample Loop Volume</td>
<td>0.5 ml (Approx.)</td>
</tr>
<tr>
<td>Columns</td>
<td></td>
</tr>
<tr>
<td>HayeSepN</td>
<td>4 ft X 1/8 in</td>
</tr>
<tr>
<td>Carboxen 1000</td>
<td>8 ft X 1/8 in</td>
</tr>
<tr>
<td>Column Temperature</td>
<td>160°C</td>
</tr>
<tr>
<td>TCD Temperature</td>
<td>63°C</td>
</tr>
<tr>
<td>FID Temperature</td>
<td>250°C</td>
</tr>
<tr>
<td>Methanizer Temperature</td>
<td>380°C</td>
</tr>
<tr>
<td>Carrier Gas Flow Rate (CG1 and CG2)</td>
<td>37.9 cm³/min</td>
</tr>
</tbody>
</table>

Figure 4.5 Calibration Curve and Regression Equation of CO₂ for FID Area

\[ y = 1.49E-14x^2 + 1.30E-07x \]

\[ R^2 = 9.91E-01 \]

fed into the reactor at 228(or 114) cm³ (STP)/min and Snoop leak detector was used to check for leaks at all connections. All feed lines were then heated above the saturation
temperature of water vapor at 1 atm. At the same time, temperature was increased to the
desired calcination temperature. The reaction began with calcination of NaHCO₃,
followed by carbonation. Product gas passed through an ice bath condenser to remove
excess water, and then to the GC sampling valve where a sample was taken every 12
minutes. The calcination temperature used in the fixed-bed reactor tests was 120°C and
the heating rate was the same as with the TGA, i.e., 5°C/min from 25°C to 100°C and
then 1°C/min from 100°C to 120°C. After about 5 to 6 hours, no more CO₂ was liberated,
which meant that calcination was complete. Then the temperature was decreased to the
desired carbonation temperature (60°C, 70°C, or 80°C) at a rate of 2°C/min. The
carbonation gas, composed of N₂, CO₂ and H₂O, was fed into the reactor when the
desired carbonation temperature was reached.

H₂O vapor was obtained in the early runs by using a syringe pump and heating the
feed lines to vaporize it. However, the low carbonation temperature made it difficult to
vaporize the water and provide just the right amount of preheat energy. With too much
preheat energy the combined gas temperature exceeded the desired carbonation
temperature; with too little preheat energy vaporization was extremely slow and
sometimes incomplete.

In later runs, steam was generated by passing the mixed N₂ and CO₂ through a gas
wash bottle contained in a water bath at 56°C, which is the temperature needed to obtain
a saturation partial pressure of 0.16 atm. The feed lines downstream of the wash bottle
were heated to prevent water from condensing. The typical carbonation test lasted about 7
to 8 hours until no more CO₂ was removed. At the end of the test, liquid water was
drained from the condenser and the volume measured for approximate material balance check.

**4.6 Materials**

Six sodium-based sorbents were used in this research. Four grades of sodium bicarbonate (SBC, NaHCO₃) were supplied by Church and Dwight (C&D) and designated as grades 1, 3, 4, and 5, and two grades of trona (natural sodium sesquicarbonate, Na₂CO₃•NaHCO₃•2H₂O) were supplied by Solvay Minerals and designated T-50 and T-200.

Table 4.4 [Green et al., 2001] describes the six sorbents. All SBC samples were 100% pure and the primary difference was the particle size. The Trona samples differed both in purity and particle size.

**Table 4.4 Sorbent Precursor Descriptions [Green et al., 2001]**

<table>
<thead>
<tr>
<th>Sorbent Precursor</th>
<th>Main Component</th>
<th>Manufacturer</th>
<th>Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBC Grade #1 USP Powdered</td>
<td>NaHCO₃</td>
<td>C&amp;D</td>
<td>100%</td>
</tr>
<tr>
<td>SBC Grade #2 USP Fine Granular</td>
<td>NaHCO₃</td>
<td>C&amp;D</td>
<td>100%</td>
</tr>
<tr>
<td>SBC Grade #3 USP Fine Powered</td>
<td>NaHCO₃</td>
<td>C&amp;D</td>
<td>100%</td>
</tr>
<tr>
<td>SBC Grade #5 USP Coarse Granular</td>
<td>NaHCO₃</td>
<td>C&amp;D</td>
<td>100%</td>
</tr>
<tr>
<td>Trona T-50</td>
<td>Na₂CO₃•NaHCO₃•2H₂O</td>
<td>Solvay</td>
<td>93.5%</td>
</tr>
<tr>
<td>Trona T-200</td>
<td>Na₂CO₃•NaHCO₃•2H₂O</td>
<td>Solvay</td>
<td>97.5%</td>
</tr>
</tbody>
</table>

Particle size, BET surface area, and mercury porosimetry data of fresh and calcined NaHCO₃ samples were measured by Research Triangle Institute, and are given in Table 4.5 [Green et al., 2001]. Composition, bulk density and particle size of the two
Trona samples were provided by Solvay [Solvay 2000 and Solvay 1998]. Mercury porosimetry data for fresh and calcined trona samples were measured at Research Triangle Institute [Green et. al., 2001]. These technical data are given in Tables 4.6.

Table 4.5 Structural Properties of Fresh and Calcined Sodium Bicarbonate Materials [Green et. al., 2001]

<table>
<thead>
<tr>
<th>SBC Grade</th>
<th>Particle Size Arithmetic Mean Microns</th>
<th>Surface Area (m²/g)</th>
<th>Mercury Porosimetry Data</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Total Intrusion Volume ml/g</td>
</tr>
<tr>
<td>Fresh</td>
<td>60.7</td>
<td>1.3</td>
<td>0.0454</td>
</tr>
<tr>
<td>Calcined overnight at 125°C in air</td>
<td>60.2</td>
<td>2.5</td>
<td>0.3908</td>
</tr>
<tr>
<td>Fresh</td>
<td>100.2</td>
<td>5.2</td>
<td>0.0295</td>
</tr>
<tr>
<td>Calcined overnight at 125°C in air</td>
<td>104.4</td>
<td>2.4</td>
<td>0.3562</td>
</tr>
<tr>
<td>Fresh</td>
<td>31.6</td>
<td>3.7</td>
<td>– – –</td>
</tr>
<tr>
<td>Calcined 3 hours at 125°C in air</td>
<td>– – –</td>
<td>3.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Calcined overnight at 125°C in air</td>
<td>33.3</td>
<td>2.7</td>
<td>0.775</td>
</tr>
<tr>
<td>Fresh</td>
<td>169.4</td>
<td>5.9</td>
<td>– – –</td>
</tr>
<tr>
<td>Calcined 3 hours at 125°C in air</td>
<td>– – –</td>
<td>2.1</td>
<td>0.1138</td>
</tr>
<tr>
<td>Calcined overnight at 125°C in air</td>
<td>170.3</td>
<td>2.5</td>
<td>0.358</td>
</tr>
</tbody>
</table>

The average particle size of NaHCO₃ samples did not changed significantly upon calcination. The BET surface areas of the fresh NaHCO₃ varied from 1.3 to 5.9 m²/g, with grade 1 having the lowest surface area of 1.3 m²/g. After overnight calcination, the
Table 4.6 Technical Data of Trona T-50 and T-200 [Solvay 2000, Solvay 1998, and Green *et al.*, 2001]

<table>
<thead>
<tr>
<th>Component</th>
<th>Typical Analysis</th>
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<th></th>
</tr>
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<tbody>
<tr>
<td></td>
<td>T-50</td>
<td>T-200</td>
<td></td>
</tr>
<tr>
<td>Na₂CO₃•NaHCO₃•2H₂O, %</td>
<td>93.5</td>
<td>97.5</td>
<td></td>
</tr>
<tr>
<td>Free Moisture, %</td>
<td>0.01</td>
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<td></td>
</tr>
<tr>
<td>H₂O Insoluble, %</td>
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<td></td>
</tr>
<tr>
<td>NaCl, %</td>
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<td>0.1</td>
<td></td>
</tr>
<tr>
<td>PH (1% solution)</td>
<td>10.1</td>
<td>– – –</td>
<td></td>
</tr>
<tr>
<td>Mercury Porosimetry Data</td>
<td>Fresh</td>
<td>Calcined overnight at 125°C in air</td>
<td>Fresh</td>
</tr>
<tr>
<td>Total Intrusion Volume, ml/g</td>
<td>0.0294</td>
<td>0.2517</td>
<td>0.3481</td>
</tr>
<tr>
<td>Average Pore Diameter (4V/A), Å</td>
<td>162</td>
<td>1074</td>
<td>938</td>
</tr>
<tr>
<td>Bulk Density, g/ml</td>
<td>2.03</td>
<td>1.58</td>
<td>1.17</td>
</tr>
<tr>
<td>Porosity, %</td>
<td>6.0</td>
<td>39.8</td>
<td>40.6</td>
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</table>

<table>
<thead>
<tr>
<th>U.S. Mesh Screen Sizes</th>
<th>Typical Cumulative Weight Percent</th>
<th>Sieve Opening</th>
<th>Typical Weight Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>T-50</td>
<td>T-200</td>
<td></td>
<td></td>
</tr>
<tr>
<td>+20</td>
<td>34</td>
<td>&lt;70 μm</td>
<td>75</td>
</tr>
<tr>
<td>+40</td>
<td>68</td>
<td>&lt;28 μm</td>
<td>50</td>
</tr>
<tr>
<td>+100</td>
<td>94</td>
<td>&lt;6 μm</td>
<td>10</td>
</tr>
<tr>
<td>+140</td>
<td>98</td>
<td>– – –</td>
<td>– – –</td>
</tr>
<tr>
<td>-140</td>
<td>2</td>
<td>– – –</td>
<td>– – –</td>
</tr>
</tbody>
</table>
surface areas of grades 2, 3, and 5 decreased while that of grade 1 increased. As a result, the surface areas of all NaHCO\textsubscript{3} materials calcined overnight converged to approximately 2.6 m\textsuperscript{2}/g.

The porosities of the fresh materials increased by a factor of 5 to 8 after overnight calcination for two grades of NaHCO\textsubscript{3}, as well as for the coarser grade of Trona (T-50). The porosities of the four grades of NaHCO\textsubscript{3} after overnight calcination in air at 125\textdegree C are relatively consistent at 46 to 55 percent. The grade 3 material developed the greatest porosity and the largest pore diameter. The Trona samples reached porosities of 39.8 and 59.5 percent after calcination, and the T-200 material had a greater average pore diameter than any of the NaHCO\textsubscript{3} materials.

For the two grades of NaHCO\textsubscript{3} tested after calcination for both 3 hours and overnight, the porosity continued to increase with increasing calcination time. For example, the porosity of the grade 5 material was more than doubled between the 3-hour sample and overnight sample. The average pore diameter also increased with extended calcination time for grade 5 while it decreased slightly for the grade 3 material. The porosities and pore volumes of the calcined NaHCO\textsubscript{3} and Trona materials were comparable, although the pores of the calcined T-200 are much larger than those of any other samples.
Chapter 5
Experimental Results and Discussion: Single Cycle Tests Using TGA

This chapter presents the results of the single-cycle tests that were completed using the TGA. Discussion examines the effects of different sorbent samples, carbonation temperature, carbonation gas composition, and calcination temperature and atmosphere. Reproducibility and hydrate formation are also studied in this chapter.

5.1 Typical Electrobalance (TGA) Test

A test using SBC Grade 3 sorbent under base case calcination and carbonation conditions is used as an example to describe a typical, single-cycle, electrobalance test. An initial charge of approximately 75 mg of sorbent precursor was heated from room temperature to 100°C at a rate of 5°C/min and from 100°C to the final calcination temperature of 120°C at a rate of 1°C/min under flowing He. After calcination was complete, which was indicated by constant weight, the temperature was decreased to the desired carbonation temperature of 70°C at a rate of 1°C/min under flowing He. The gas composition was then changed to 8% CO₂, 16% H₂O and balance He at a total flow rate of 600 sccm for carbonation. Carbonation was continued until the reaction rate approached zero, which was indicated by constant weight. System pressure was 1atm during calcination and carbonation.

The response curve is presented in Figure 5.1, where dimensionless sorbent weight and temperature are shown as a function of time. Decomposition of NaHCO₃ to Na₂CO₃ began at about 100°C and was complete soon after the final calcination temperature of 120°C was reached. The final dimensionless weight is quite near the theoretical value of 0.631 that is indicated by the horizontal dashed line.
The temperature was then decreased to the 70°C carbonation temperature. CO\(_2\) and H\(_2\)O were added after about 190 min to produce the desired carbonation gas composition at a total flow rate of 600 sccm. The dimensionless weight increase corresponded to the removal of CO\(_2\) from the gas phase via the conversion of Na\(_2\)CO\(_3\) to the carbonation products. The global reaction rate, which is related to the slope of the dimensionless weight-time curve, began at a high value, decreased with time, and approached zero after about 325 min.

From the HSC thermodynamic analysis, the carbonation product should be NaHCO\(_3\) under the carbonation conditions. Complete carbonation would produce a final dimensionless weight of 1.0 if the product was NaHCO\(_3\) and fractional carbonation as a function of time, \(f(t)_{\text{abc}}\), can be calculated from
\[ f(t)_{sbc} = \frac{d_w(t) - 0.631}{0.369} \tag{5.1} \]

where \( d_w(t) \) is the dimensionless weight at time \( t \) after the beginning of carbonation. In this example test \( f(200)_{sbc} \) is approximately 0.60.

The response curves for Trona T-50 and T-200 are similar to SBC 3 except the decomposition rate is faster and the final theoretical calcination dimensionless weights are different (0.723 for T-50 and 0.711 for T-200).

### 5.2 Wegscheider’s Salt

Carbonation products from the fixed-bed reactor (to be discussed later) at base case calcination and carbonation conditions (except that \( N_2 \) was substituted for He) were analyzed by Church and Dwight. X-ray diffraction analysis showed that the products were approximately 85% Wegscheider’s salt (\( Na_2CO_3 \cdot 3NaHCO_3 \)) and balance sodium carbonate (\( Na_2CO_3 \)) [Green, et. al., 2002].

The proposed reason for forming Wegscheider’s salt is that the exothermic carbonation reaction caused the temperature of the sample to be higher than the nominal reaction temperature. The thermodynamic analysis (see Chapter 3) showed that higher temperature is favorable to the formation of Wegscheider’s salt.

The fractional carbonation as a function of time on the basis of Wegscheider’s salt product, \( f(t)_{ws} \), can be calculated from

\[ f(t)_{ws} = \frac{d_w(t) - 0.631}{0.221} \tag{5.2} \]

By ratioing equations (5.1) and (5.2)

\[ f(t)_{ws} = 1.67 f(t)_{sbc} \tag{5.3} \]
Thus \( f(200)_{ws} \) in the example test is approximately 1.0, \( i.e. \) 100\% conversion of \( \text{Na}_2\text{CO}_3 \) to \( \text{Na}_2\text{CO}_3\cdot3\text{NaHCO}_3 \).

The equations for the fractional carbonation, \( f(t)_{ws} \), for Trona T-50 and T-200 based on Wegscheider’s salt formation are

\[
f(t)_{ws,T-50} = \frac{dw(t) - 0.723}{0.231} \quad (5.4)
\]

\[
f(t)_{ws,T-200} = \frac{dw(t) - 0.711}{0.241} \quad (5.5)
\]

The coefficients are determined from the stoichiometric equations, equations 3.3 and 3.4, and the impurity levels of the Trona samples (Table 4.6). While the equations relating dimensionless weight and \( f(t)_{sbc} \) and \( f(t)_{ws} \) for T-50 and T-200 are somewhat different, the ratio of fractional carbonation \( f(t)_{ws} \) to \( f(t)_{sbc} \) is the same as given in equation 5.3.

5.3 Reproducibility

Reproducibility of duplicate tests at base case conditions using SBC Grade 3 and Trona T-50 are presented in Figures 5.2 and 5.3.

Figure 5.2 shows the dimensionless weight as a function of time during the carbonation of the three duplicate tests using SBC sorbent Grade 3. Those tests were conducted at base case calcination and carbonation conditions. Electrobalance noise shown in Figure 5.1 has been removed by smoothing the data so that the individual test results may be distinguished clearly. While there is some variation in initial rates, the overall results are quite reproducible, and each of the final dimensionless weights are effectively equal to 0.84, which corresponds to 94.6\% carbonation for Wegscheider’s salt (\( \text{Na}_2\text{CO}_3\cdot3\text{NaHCO}_3 \)) product. The duplicate tests using SBC Grade 1 produced similar reproducibility.
Figure 5.2 Duplicate Carbonation Tests Using SBC Grade 3 at 70°C

Results of duplicate tests using Trona T-50 are presented in Figure 5.3. All three tests used base case calcination and carbonation conditions. Results from two tests are effectively identical, but the third shows significantly larger initial rate and larger final dimensionless weight. The final dimensionless weight in the two identical tests corresponded to about 80% carbonation while the final carbonation in the third test was about 83.5% (based on Wegscheider’s salt product). In general, duplicate tests using Trona suffered from poor reproducibility.

The duplicate Trona tests used randomly acquired samples of as-received sorbent precursor. Variations in composition due to impurities and/or particle size were considered to be possible causes of the poor reproducibility. While impurity variations could not be eliminated, the possible effect of variable particle size was eliminated by sieving the as-received sorbent and selecting the 60-70 mesh size range for testing. Three duplicate tests using base case reaction conditions with the exception of 80°C
carbonation temperature were carried out using sieved Trona T-50. Results are shown in Figure 5.4 along with the results of a previous test conducted at the same reaction conditions but using the as-received T-50 (indicated by the dashed line). There is a considerable range in initial rates with the unsieved material showing the highest initial rate. Two tests using sieved precursor gave approximately the same initial rates while one test produced a significantly lower initial rate. Final dimensionless weights were all approximately equal and ranged only from 0.91 to 0.92, corresponding to 80% to 83.5% carbonation. We concluded that particle size variations were not the cause of the Trona reproducibility problems.

5.4 Formation of Sodium Carbonate Monohydrate (Na$_2$CO$_3$•H$_2$O)

The direct formation of hydrate via the reaction

$$\text{Na}_2\text{CO}_3 (s) + \text{H}_2\text{O} (g) \rightarrow \text{Na}_2\text{CO}_3\cdot\text{H}_2\text{O} (s)$$
Figure 5.4 Duplicate Carbonation Tests Using Sieved Trona T-50 at 80°C

is thermodynamically favored at some of the carbonation conditions of interest. The occurrence of simultaneous gas-solid reactions makes the quantitative interpretation of electrobalance results impossible. Hence a number of runs using an H₂O/He atmosphere were carried out to study hydrate formation.

Figure 5.5 presents the smoothed dimensionless weight versus time results for a series of runs using SBC Grade 3 with a gas composition of 10% H₂O, balance He at temperatures between 50°C and 70°C. The increases in weight at 50°C and 60°C are indicative of hydrate formation, while the constant weight at 65°C and 70°C show that no hydrate is formed at these temperatures. The horizontal dashed line at dimensionless weight of 0.63 corresponds to the theoretical value for complete calcination. All initial values were quite close to the theoretical value. The wavy nature of the curve at 60°C is attributed to the data smoothing procedure.
Figure 5.5 Hydrate Formation in the Presence of 10% H\textsubscript{2}O using SBC Grade 3

Complete conversion of Na\textsubscript{2}CO\textsubscript{3} to Na\textsubscript{2}CO\textsubscript{3}\textbullet H\textsubscript{2}O corresponds to a final dimensionless weight of 0.74, which is very close to the final experimental value at 50°C. Thermodynamic calculations using HSC Chemistry show that 59°C is the maximum temperature where hydrate formation is favored in this gas composition, while the experimental results indicate that hydrate formation is possible at 60°C and impossible at 65°C. Thus the experimental results and thermodynamic calculations are in reasonable, but not perfect, agreement.

The H\textsubscript{2}O content was increased to 16% and dimensionless weight versus time results are shown in Figure 5.6. A small amount of hydrate was formed at 65°C but no hydrate was formed at 70°C. This result is consistent with HSC Chemistry calculations that show 66°C is the maximum temperature for hydrate formation at this higher H\textsubscript{2}O concentration. The predicted H\textsubscript{2}O concentration required for hydrate formation at 70°C is
Figure 5.6 Hydrate Formation in the Presence of 16% H₂O using SBC Grade 3

19.5%, which is above the maximum value of interest.

5.5 Detailed Parametric Tests

5.5.1 Sorbent Precursors

Figure 5.7 compares the dimensionless weight versus time response during the carbonation cycle for three sorbents—SBC Grades 1 and 3, and Trona T-50—for a reaction temperature of 60°C. The initial dimensionless weights are very close to the theoretical values of 0.631 for SBC, 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, as measured by the slopes of the curves between \( t = 0 \) and \( t = 25 \) min, are approximately equal. The final dimensionless weights for the two SBC samples are also reasonably close. The larger final value of dimensionless weight for Trona T-50 does not necessarily correspond to increased fractional carbonation since the final dimensionless weight
corresponding to complete carbonation of Trona T-50 is 0.95 (based on Na$_2$CO$_3$•3NaHCO$_3$) or 1.11 (based on NaHCO$_3$) while for SBC samples complete carbonation corresponds to 0.85 (based on Na$_2$CO$_3$•3NaHCO$_3$) or 1.0 (based on NaHCO$_3$).

5.5.2 Carbonation Temperature

Carbonation temperature affects both kinetics and thermodynamics of the reaction. Figure 5.8 compares smoothed results for three tests using SBC Grade 3 at temperatures of 60°C, 70°C, and 80°C, all using base case calcination conditions and base case carbonation gas composition with a carbonation gas flow rate of 300 sccm. Both the initial rate of reaction, as measured by the initial slope of the dimensionless weight-time curve, and the final dimensionless weight increased with decreasing temperature. The reaction rate approached zero after about 200 min of carbonation at both 60°C and 70°C,
while the reaction rate at 80°C was approximately constant until about 350 min and then approached zero.

Figure 5.9 also shows the effect of carbonation temperature on reaction rates and achievable sorbent capacities using SBC Grade 3, but exposed to a different gas composition. The carbonation gas contained 5% CO₂, 16% H₂O and balance He. Reaction occurred at both 60°C and 70°C, but there was no reaction at 80°C. HSC Chemistry predicts that at 80°C with an H₂O pressure of 0.16 atm, NaHCO₃ may be formed at CO₂ pressure of 0.026 atm or higher. In addition, the maximum temperature for the formation of Na₂CO₃•3NaHCO₃ using this gas composition is 81°C. Thus, while the formation of NaHCO₃ and Na₂CO₃•3NaHCO₃ were thermodynamically possible at 80°C, no reaction occurred. The probable reason is that the temperature of the solid sample was higher than that of the bulk gas because of the exothermic reaction.
Figure 5.9 Effect of Temperature in a Carbonation Gas Containing 5% CO₂ and 16% H₂O Using SBC Grade 3

Figure 5.10 shows the effect of carbonation temperature using as-received Trona T-50. Base case calcination conditions and carbonation gas compositions were used, with a carbonation gas flow rate of 300 sccm. Initial dimensionless weights were all quite close to the theoretical value of 0.723 for T-50, presented as the horizontal dashed line, indicating that complete calcination was always obtained. The initial rate was highest at 80°C, somewhat lower at 70°C, and a minimum at 60°C. This is counter to the results for SBC Grade 3 where the initial rate decreased with increasing temperature. The maximum final dimensionless weight occurred at 60°C, with both 70°C and 80°C results showing approximately the same final values. In contrast, the final dimensionless weight decreased with increasing temperature using SBC Grade 3.

The final dimensionless weight of 0.92 at 70°C and 80°C corresponds to about 50% carbonation based on NaHCO₃ product and about 83% for Na₂CO₃•3NaHCO₃,
Figure 5.10 Effect of Carbonation Temperature in a Base Case Carbonation Gas Composition at a Flow Rate of 300 sccm Using Trona T-50

while the final dimensionless weight of 0.98 at 60°C corresponds to about 65% or 108% carbonation for NaHCO$_3$ and Na$_2$CO$_3$•3NaHCO$_3$ respectively.

The effect of carbonation temperature for Trona T-50 at a higher flow rate of 600 sccm is shown in the Figure 5.11. The sorbent precursor, gas composition and temperatures were the same as those in Figure 5.11. In this case the initial rate was in the order of 70°C > 80°C > 60°C, while carbonation at both 60°C and 70°C resulted in final dimensionless weight of 0.94 compared to 0.91 at 80°C. These values correspond to final fractional carbonations of 49% and 55% (based on NaHCO$_3$) or 81% and 92% (based on Na$_2$CO$_3$•3NaHCO$_3$), respectively.

The order of the initial rates is quite different from that observed at 300 sccm (Figure 5.10). Additionally, the final dimensionless weight at 60°C is considerably lower than that observed from the 300 sccm data, while those at both 70°C and 80°C are about
equal to those observed at 300 sccm. These unexpected results provided further evidence of the lack of reproducibility with the T-50 samples.

The decreasing rate with increasing temperature observed with SBC 3 is attributed to reaction reversibility. The carbonation reaction is exothermic and equilibrium fractional CO$_2$ removal decreases with increasing temperature as indicated by Figure 3.5. It is reasonable that the reaction rate is proportional to the difference between CO$_2$ concentration in the bulk gas ($C_0$) and equilibrium CO$_2$ concentration at that temperature ($C_e$). This difference can be calculated from the following equation:

$$C_0 - C_e = \frac{(y_0 - y_e)P}{RT}$$

where: $y_0$ – bulk mole fraction of CO$_2$

$y_e$ – equilibrium mole fraction of CO$_2$
$P$ – pressure

$R$ – gas constant, $R = 1.987 \text{ cal/(K\cdot mol)} = 8.314 \text{ J/(K\cdot mol)}$

$T$ – temperature in K

Thus, the differences at temperatures used in above tests (Figures 5.8 to 5.11) are:

- $T = 60^\circ\text{C}$  \hspace{1cm} $C_0 - Ce = 0.0028 \text{ mol/L}$
- $T = 70^\circ\text{C}$  \hspace{1cm} $C_0 - Ce = 0.0025 \text{ mol/L}$
- $T = 80^\circ\text{C}$  \hspace{1cm} $C_0 - Ce = 0.0016 \text{ mol/L}$

Therefore, the CO$_2$ reaction driving force is reduced by more than 40 percent at 80$^\circ$C compared to that at 60$^\circ$C.

### 5.5.3 CO$_2$ Concentration

The effect of CO$_2$ concentration on SBC Grade 3 carbonation is shown in Figure 5.12. Standard calcination conditions were used and carbonations were carried out at 70$^\circ$C along with a flow rate of 300 sccm. A fixed 16% H$_2$O, as well as 0%, 5% and 8% CO$_2$, were used to test the effect of CO$_2$ concentration. Figure 5.12 shows that increasing the CO$_2$ concentration at constant temperature and H$_2$O concentration produced a measurable increase in the reaction rate. The sorbent capacity after 250 min was also greater in 8% CO$_2$; however, extrapolation of the dimensionless weight-time curves for 8% and 5% CO$_2$ suggests that the ultimate achievable capacity for the two runs would be approximately equal.

Figure 5.13 presents the effect of CO$_2$ concentration on carbonation of Trona T-50 with carbonation at constant temperature of 70$^\circ$C, H$_2$O concentration of 16%, flow rate of 600 sccm, and CO$_2$ concentrations of 5%, 8% or 10%. Standard calcination conditions were used in all three tests.
Figure 5.12 Effect of CO$_2$ Concentration for SBC Grade 3

Figure 5.13 Effect of CO$_2$ Concentration for Trona T-50
The initial rates were approximately equal at 8% and 10% CO\textsubscript{2}, and considerably larger than at 5% CO\textsubscript{2}. However, the final dimensionless weight using 5% CO\textsubscript{2} was significantly larger and corresponded to a final carbonation conversion of about 65\% (NaHCO\textsubscript{3}) or 108\% (Na\textsubscript{2}CO\textsubscript{3}•3NaHCO\textsubscript{3}). The final carbonation conversions using 8\% and 10\% CO\textsubscript{2} were about 50\% and 45\% for NaHCO\textsubscript{3} product, or 83\% and 75\% for Na\textsubscript{2}CO\textsubscript{3}•3NaHCO\textsubscript{3}, respectively.

The most obvious difference in the Figure 5.13 results is the fact that, in spite of the lower initial rate for 5\% CO\textsubscript{2}, reaction continued for a much longer time. Dimensionless weights were equal at about 80 min, but the reaction was still occurring slowly after 190 min in 5\% CO\textsubscript{2}. Similar results in other gas-solid noncatalytic reactions have been explained on the basis of higher reaction rates associated with higher CO\textsubscript{2} concentrations causing more rapid pore closure. Lower reaction rate at lower CO\textsubscript{2} concentration distributes the reaction in a broader zone within the sorbent particle, and postpones or even avoids pore closure.

### 5.5.4 H\textsubscript{2}O Concentration

The effect of H\textsubscript{2}O concentration on carbonation of SBC Grade 3 and Trona T-50 were examined and results are shown in Figures 5.14 and 5.15. Carbonations were carried out at 300 sccm with H\textsubscript{2}O contents of 10\% and 16\% for SBC Grade 3, and at 600 sccm with H\textsubscript{2}O contents of 5\%, 10\% and 16\% for Trona T-50. Other carbonation conditions, as well as calcination conditions, were standard.

Figure 5.14 shows that increasing H\textsubscript{2}O concentration at constant temperature and CO\textsubscript{2} concentration produced an increase in the reaction rate, while the final achievable capacity was approximately the same at both H\textsubscript{2}O contents.
Figure 5.14 Effect of H$_2$O Concentration for SBC Grade 3

Figure 5.15 Effect of H$_2$O Concentration for Trona T-50
The results for Trona T-50 in Figure 5.15 show the same effect of the H$_2$O concentration on the reaction rate as for SBC Grade 3. However, the final dimensionless weight was approximately equal in 5% and 10% H$_2$O, and somewhat larger in 16% H$_2$O.

5.5.5 Calcination Temperature and Atmosphere

Standard calcination conditions of 120°C in He were chosen to minimize the severity of sorbent exposure. In commercial practice, however, calcination would occur in an atmosphere having a high CO$_2$ content and perhaps at a temperature substantially higher than 120°C. A series of tests using a pure CO$_2$ calcination atmosphere and with the calcination temperatures ranging from 120°C to 200°C was carried out. The effect of calcination conditions was then observed by comparing the results from the subsequent carbonation cycle using standard carbonation conditions.

Carbonation results using SBC Grade 3 following calcination in pure CO$_2$ at four temperatures are compared in Figure 5.16 with carbonation results following calcination under standard conditions of 120°C in He. There is essentially no difference in the initial reaction rates. The dimensionless weight-time curves are almost identical for the first 50 minutes. Thereafter there is a small spread in the results, but the final dimensionless weights vary only between 0.85 and 0.87, corresponding to final carbonations between 59% and 65% (based on NaHCO$_3$), or 99% and 108% (based on Na$_2$CO$_3$•3NaHCO$_3$). Thus it is clear that calcination at a temperature as high as 200°C in pure CO$_2$ has little, if any, negative effect on single cycle carbonation performance.

Tests using a calcination atmosphere containing 80% CO$_2$ and 20% H$_2$O were carried out at temperatures of 150°C and 200°C. Results of the subsequent carbonation cycle are compared to results using standard calcination conditions of 120°C in He in
Figure 5.16 Effect of Calcination Temperature in Pure CO$_2$ for SBC Grade 3

Figure 5.17. Once again, results from all three runs are quite close. If anything, the two carbonation tests following higher temperature calcination in CO$_2$/H$_2$O produced slightly higher final dimensionless weights. Clearly, higher temperature calcination in the CO$_2$/H$_2$O atmosphere had little effect on single cycle carbonation performance.

5.6 Conclusions

- Single cycle test results show that SBC samples exhibited quite good reproducibility, while Trona samples did not.
- Hydrate formation was favored at lower temperatures and higher H$_2$O contents in the absence of CO$_2$.
- SBC Grades 1 and 3 had higher capacities than Trona T-50.
- Reaction rate and final achievable capacity decreased with increasing carbonation temperature for SBC samples, which agrees with the thermodynamic analysis.
Figure 5.17 Effect of Calcination Temperature in 80% CO$_2$/20% H$_2$O for SBC Grade 3

- Reaction rate and final achievable capacity increased with increasing concentration of both CO$_2$ and H$_2$O for SBC samples.

- Calcination temperature and atmosphere had little effect on the subsequent carbonation results using SBC Grade 3 sorbent.

- Reproducibility of tests using Trona samples was poor and firm conclusions of the effects of temperature and gas composition were not possible.
Multi-cycle tests were conducted to test sorbent durability and activity maintenance through several calcination-carbonation cycles. Such information provides preliminary information about the economical viability of this CO$_2$ capture concept.

This chapter presents the results of the multi-cycle tests that were completed using the TGA. All multi-cycle tests, mostly five cycles, used standard carbonation conditions while calcination conditions were varied. Discussion will be presented on the effects of calcination temperature and atmosphere, the number of calcination-carbonation cycles, and the presence of contaminants on reaction rate and achievable sorbent capacity.

### 6.1 Typical Five-Cycle Test and Effect of Cycle Numbers

Raw electrobalance results from a five-cycle test using SBC Grade 3 using base calcination and carbonation conditions are shown in Figure 6.1. The initial charge was NaHCO$_3$ having a dimensionless weight of 1.0. Initial calcination was complete after about 80 minutes as indicated by the constant dimensionless weight of 0.63, which was achieved at the end of all five calcination steps. The first carbonation was initiated at about 200 minutes and continued until the dimensionless weight approached a constant value. In this test the sample was left overnight at 70°C in pure He after calcination cycles 2 and 4, and the subsequent carbonation and calcination occurred the next day. The time scale shown in Figure 6.1 is arbitrary following the first cycle.

Figure 6.1 clearly shows a decrease in the final dimensionless weight near the end of each carbonation cycle (except cycle 3), as well as small decreases in the slopes of the dimensionless weight-time curves near the beginning of carbonation. Both are indicative
of decreased activity with increasing cycle number. These results are indicated more clearly in Figure 6.2 where smoothed electrobalance data for the first 150 min carbonation during the five cycles are overlaid. Both the reduced initial slope and reduced final dimensionless weight are clear.

The dimensionless weight after 150 min of 0.87 in carbonation cycle 1, corresponding to fractional carbonation of 108% based on Na$_2$CO$_3$•3NaHCO$_3$ product, was in reasonable agreement with previous single cycle results. The 150-minute dimensionless weight obviously decreased from 0.87 in cycle 1 to 0.82 and 0.81 in cycles 2 and 3, corresponding to 86% and 81% carbonation. The 150-minute dimensionless weights in cycles 4 and 5 were about 0.80, corresponding to about 76% carbonation.

Similar smoothed dimensionless weight-time data for five carbonation cycles using base reaction conditions for Trona T-200 are presented in Figure 6.3. There was no
Figure 6.2 Smoothed Electrobalance Data for Five Carbonation Cycles Using SBC Grade 3 with Base Reaction Conditions

Figure 6.3 Smoothed Electrobalance Data for Five Carbonation Cycles Using Trona T-200 and Base Reaction Conditions
significant difference in either the initial reaction rate or final fractional carbonation, indicated by the slope and final dimensionless weight, respectively, among all five cycles. Comparing Figures 6.2 and 6.3, the initial reaction rates for Trona T-200 were higher than those for SBC Grade 3, which resulted in a faster approach to constant dimensionless weight for Trona T-200.

6.2 Reproducibility

The fractional conversion of $\text{Na}_2\text{CO}_3$ to $\text{Na}_2\text{CO}_3\cdot3\text{NaHCO}_3$ at selected times was used to facilitate comparison of results from different runs. The fractional conversion, $f(t)$, as a function of time is given by equations (5.2), (5.4), and (5.5) in Chapter 5 corresponding to SBC, Trona T-50, and T-200 samples, respectively. Values of $f(25)$ and $f(150)$ were chosen as a measure of reaction rate and final conversion.

Reproducibility of test results under identical reaction conditions for SBC Grade 3 is shown in Figure 6.4 where $f(25)$ and $f(150)$ are plotted versus cycle number. Three different SBC Grade 3 samples were subjected to five complete cycles at standard reaction conditions. The discrete points represent the results from individual runs with different symbols used to distinguish different tests, and the solid lines indicate the average values of the three runs. It is obvious that a great deal of scatter exists between the runs, particularly with respect to $f(25)$. In addition, there is no consistent trend as the largest single value of $f(25)$ occurred in cycle 4 in one of the runs. The $f(150)$ results show less scatter and there is a clear decrease from cycles 1 to 2 to 3 for all runs. However, the final conversion is reasonably constant in cycles 3, 4, and 5. The average value of $f(150)$ in cycle 5 is 23% less than in cycle 1.
Similar reproducibility results for three duplicate tests using Trona T-200 at standard reaction conditions are shown in Figure 6.5. The discrete points represent the individual test results and the line is drawn through the average values. It is immediately evident that there is even more scatter for \( f(25) \) than shown in Figure 6.4, which confirms the variability between Trona samples seen in single-cycle tests. The triangles represent the run shown in Figure 6.3. Moreover, there is no consistent trend for both \( f(25) \) and \( f(150) \) even though the average initial rate and final carbonation were most favorable in cycle 1. The average \( f(150) \) value in cycle 5 was 11% less than in cycle 1 for T-200, which is smaller than SBC Grade 3 results. Therefore, while Trona T-200 appears to be more stable with increasing cycle number than SBC Grade 3, this result cannot be confirmed because of the variability between Trona samples.
6.3 Effect of Calcination Temperature and Atmosphere

The effects of calcination temperature and atmosphere on sorbent reactivity and capacity are compared on the basis of $f(25)$ and $f(150)$. Results from four different calcination conditions using SBC Grade 3 are shown in Figures 6.6 and 6.7. Average values of $f(25)$ and $f(150)$ are plotted for duplicate runs using calcination conditions of 120°C in He (from Figure 6.4) and 200°C in CO$_2$ (three runs).

$f(25)$ values for calcination in He at 120°C were larger than those at the other three conditions throughout the five cycles. Calcination in He at 120°C also produced the largest values of $f(150)$ during cycles 1 and 2, while calcination in He at 160°C had the largest $f(150)$ values for the last two cycles. $f(150)$ values for calcination in He at 120°C and in CO$_2$ at 200°C were quite similar during cycles 3, 4, and 5. Calcination in 80%CO$_2$/20%H$_2$O at 200°C produced the smallest values of $f(150)$ for all five cycles.
Figure 6.6 Comparison of $f(25)$ Results for Four Different Calcination Conditions Using SBC Grade 3

Figure 6.7 Comparison of $f(150)$ Results for Four Different Calcination Conditions Using SBC Grade 3
Figures 6.8 ($f(25)$) and 6.9 ($f(150)$) show results from three different calcination conditions using SBC Grade 1. Similar to the results of SBC Grade 3, there was no consistent trend of $f(25)$ values at any of the calcination conditions, and calcination at $120^\circ$C in He resulted in the largest $f(25)$ values during all five cycles. Figure 6.8 also clearly shows an increase in reactivity through the first three cycles followed by a small decrease in cycles 4 and 5 using calcination at $120^\circ$C in He. It is clear that higher calcination temperature has an adverse effect on multicycle reactivity, but that there is little, if any, reactivity decrease with increasing cycle number at any of the calcination conditions. It is also interesting to note that there is relatively little difference in the reactivities following calcination at $160^\circ$C in He and $200^\circ$C in CO$_2$.

![Figure 6.8 Comparison of $f(25)$ Results for Three Different Calcination Conditions Using SBC Grade 1](image)

The sorbent capacity results shown in Figure 6.9 indicate little difference of $f(150)$ values between calcination conditions of $120^\circ$C in He and $200^\circ$C in CO$_2$. 
Calcination at 160°C in He produced the smallest $f(150)$ values throughout the five cycles, which indicates that both calcination temperature and atmosphere affect carbonation. Further, after a large decrease in capacity between cycles 1 and 2 using 160°C calcination in He, there was relatively little further decrease in subsequent cycles.

Trona T-200 was used in most of the multicycle trona tests since Trona T-50 showed even poorer reproducibility than T-200. Figures 6.10 and 6.11 represent the results from six different calcination conditions using Trona T-200. The tests using 120°C in CO₂ and 140°C in CO₂ were terminated after three cycles because of reactor problems. Even though the increased calcination temperature and different atmosphere had a relatively small impact on SBC samples, Figures 6.10 and 6.11 show a clear difference between calcination temperatures of 100°C and 120°C and results using 140°C, 160°C, and 200°C calcination temperatures. The difference is particularly obvious for $f(25)$
Figure 6.10 Comparison of $f(25)$ Results for Six Different Calcination Conditions Using Trona T-200

Figure 6.11 Comparison of $f(150)$ Results for Six Different Calcination Conditions Using Trona T-200
values. Thus the adverse effect of more severe calcination conditions on T-200 performance is proven.

There appears to be a slight improvement in performance following 100°C calcination in He. The $f(25)$ results in cycles 2 through 5 and the $f(150)$ results in all cycles are quite constant.

Figures 6.12 and 6.13 present the results for Trona T-50 at three different calcination conditions. Trona T-50 was also adversely affected by the more severe calcination conditions. With the exception of the single $f(25)$ data point corresponding to cycle 3 using calcination in He at 120°C, the $f(25)$ values using base calcination conditions were larger than those using the two more severe calcination conditions, which is similar to the results for Trona T-200. Also 160°C calcination in He resulted in the smallest $f(25)$ values from cycles 3 to 5.

![Figure 6.12 Comparison of $f(25)$ Results for Three Different Calcination Conditions Using Trona T-50](image-url)
Figure 6.13 Comparison of $f(150)$ Results for Three Different Calcination Conditions Using Trona T-50

Figure 6.13 also shows that the largest $f(150)$ values were obtained with calcination at 120°C in He during all five cycles. The $f(150)$ value corresponding to calcination at 160°C in He was slightly larger than that at 200°C in CO₂ for the first cycle; thereafter $f(150)$ values for calcination at 200°C in CO₂ were larger $f(150)$.

It is clear that even moderate increases in the severity of calcination cause a significant decrease in both reactivity and capacity for both Trona samples, which is different from the results of SBC samples.

6.4 Comparison of Sorbents

Results of multicycle tests using SBC Grades 1 and 3, Trona T-50, and T-200 using base case reaction conditions are compared in Figures 6.14 and 6.15, where $f(25)$ and $f(150)$ are plotted versus cycle number. Again, average values of $f(25)$ and $f(150)$ were used for the duplicate runs using SBC Grade 3 and T-200. As shown in Figure 6.14,
Figure 6.14 Comparison of $f(25)$ Results for Four Different Sorbents Using 120°C Calcination in He

Figure 6.15 Comparison of $f(150)$ Results for Four Different Sorbents Using 120°C Calcination in He
$f(25)$ values of SBC Grade 1 were clearly the largest except during cycle 1 where SBC Grade 1 and T-200 values were essentially equal. T-50 produced the smallest $f(25)$ values throughout the five cycles, and $f(25)$ values for SBC Grade 3 were smaller than T-200 except in cycle 2, where the $f(25)$ values were about equal.

Figure 6.15 shows that SBC Grade 1 had the largest capacities for cycles 2 through 5, and that the $f(150)$ values were almost constant during those cycles. Only SBC Grade 3 showed a consistent decrease in $f(150)$ values. $f(150)$ values of SBC Grade 3 were larger than those of T-200 and T-50 during cycles 1 and 2, but were not significantly different during cycles 3 through 5.

The performance of the four sorbents — SBC Grades 1 and 3, T-50, and T-200 — using calcination conditions of 160°C in He is compared in Figures 6.16 and 6.17. SBC Grade 1 again clearly exhibited the highest reactivity while the capacities of SBC Grades 1 and 3 were approximately equal. Both SBC samples showed higher capacity than the Trona samples. Decreases in reactivity, with the exception of SBC Grade 3 between cycles 1 and 2 and T-50 between cycles 2 and 3, were moderate.

The performance of the four sorbents following calcination at 200°C in CO$_2$ is compared in Figures 6.18 and 6.19. Once again SBC Grade 1 produced the largest $f(25)$ values followed by SBC Grade 3 as shown in Figure 6.18. In addition, there was a significant difference between the $f(25)$ values for SBC Grades 1 and 3. Values of $f(25)$ for T-50 and T-200 were approximately equal but well below the values for SBC Grades 1 and 3. Overall the reactivities were reasonably constant except for the decreases with SBC Grade 1 between cycles 4 and 5 and for SBC Grade 3 between cycles 1 and 2.
Figure 6.16 Comparison of $f(25)$ Results for Four Different Sorbents Using 160°C Calcination in He

Figure 6.17 Comparison of $f(150)$ Results for Four Different Sorbents Using 160°C Calcination in He
Figure 6.18 Comparison of $f(25)$ Results for Four Different Sorbents Using 200°C Calcination in CO$_2$

Figure 6.19 Comparison of $f(150)$ Results for Four Different Sorbents Using 200°C Calcination in CO$_2$
Figure 6.19 shows a similar trend in $f(150)$ values. The capacity order was SBC-1 > SBC-3 > T-50 > T-200. All sorbents showed a moderate decrease in $f(150)$ with increasing cycle number.

### 6.5 Effect of Contaminants

The presence of SO$_2$ in the flue gas will likely interfere with CO$_2$ removal through the formation of Na$_2$SO$_3$ and/or Na$_2$SO$_4$. The anticipated reactions were discussed in Chapter 3 and are shown below.

\[
\text{Na}_2\text{CO}_3 (s) + \text{SO}_2 (g) \rightarrow \text{Na}_2\text{SO}_3 (s) + \text{CO}_2 (g) \quad (3.6)
\]

\[
\text{Na}_2\text{CO}_3 (s) + \text{SO}_2 (g) + 0.5\text{O}_2 (g) \rightarrow \text{Na}_2\text{SO}_4 (s) + \text{CO}_2 (g) \quad (3.7)
\]

The effect of SO$_2$ addition, with and without the presence of free O$_2$, was examined in a series of multicycle electrobalance tests. When 0.4% and 0.2% SO$_2$ were added the tests were terminated after three cycles, while the remaining tests in which 0.1% SO$_2$ was added were carried out through five cycles. Standard calcination conditions and carbonation temperature were used in each test. Only the carbonation gas composition was varied. CO$_2$ and H$_2$O concentrations were the same as in the base case carbonation conditions and N$_2$ was reduced by the amount of SO$_2$ added. Trona T-200 was only used in one test and the remaining tests used SBC Grade 3.

Figure 6.20 shows raw electrobalance data versus time for a three-cycle test using SBC Grade 3 in which 0.2% SO$_2$ was added to the carbonation gas. The scattered data represent the dimensionless weight, while the smoother data indicate the temperature. The initial calcination progressed as expected with a final dimensionless weight very near the theoretical value of 0.631. The dimensionless weight increased rapidly during the first carbonation cycle and reached a maximum of about 0.88 slightly more than 100
Figure 6.20 Dimensionless Weight Versus Time Showing the Effect of SO\textsubscript{2} in the Carbonation Gas: SBC Grade 3 and 0.2\% SO\textsubscript{2}

minutes later. The dimensionless weight then decreased to about 0.83 when the first carbonation cycle was ended. The final dimensionless weight at the end of the second calcination cycle was 0.68. In the second carbonation cycle the maximum dimensionless weight was only about 0.82. The minimum weight following the third calcination was 0.71 and the maximum weight at the end of the third carbonation was 0.78. When the sorbent was calcined for a fourth time the final weight decreased only to about 0.74. The calcination temperature was then increased from 120\degree C to 200\degree C in steps of 20\degree C, but there was almost no additional weight loss occurred. These results suggest the formation of increasing amounts of Na\textsubscript{2}SO\textsubscript{3} during each carbonation cycle, and further that the Na\textsubscript{2}SO\textsubscript{3} is stable in He at temperatures as high as 200\degree C.

The cause of the maximum in the dimensionless weight during a carbonation cycle, which occurred only during the first cycle, is unknown. The amount of CO\textsubscript{2}
removed in each cycle should be proportional to the difference in dimensionless weight at the end of the carbonation and subsequent calcination cycles. The difference decreased from 0.15 in cycle 1 (based on the final dimensionless weight of 0.83) to 0.11 in cycle 2 to 0.04 in cycle 3. Clearly there was little CO$_2$ removal capacity left after three cycles.

Reducing the SO$_2$ concentration to 0.1% produced qualitatively similar results as shown in Figure 6.21. However the reduction in CO$_2$ capacity occurred at a slower rate thus allowing five cycles to be completed. Also there were no dimensionless weight maxima during any of the carbonation cycles of Figure 6.21. The difference in dimensionless weight at the end of carbonation cycle 1 and calcination cycle 2 was about 0.17. At the end of four cycles this difference decreased to 0.06. These numbers suggest that the loss in CO$_2$ capacity following three cycles with 0.2% SO$_2$ was almost 75% compared to an approximate 65% loss following four cycles with 0.1% SO$_2$ in the feed gas.

![Figure 6.21 Dimensionless Weight Versus Time Showing the Effect of SO$_2$ in the Carbonation Gas: SBC Grade 3 and 0.1% SO$_2$](image)

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Results of the test using Trona T-200 with 0.1% SO\textsubscript{2} were qualitatively similar to those for SBC Grade 3 and are shown in Figure 6.22.

![Figure 6.22 Dimensionless Weight Versus Time Showing the Effect of SO\textsubscript{2} in the Carbonation Gas: Trona T-200 and 0.1% SO\textsubscript{2}](image)

Results obtained when both O\textsubscript{2} and SO\textsubscript{2} were added to the carbonation gas were not greatly different from results with SO\textsubscript{2} alone as shown in Figure 6.23. This figure shows five cycle results with 0.1% SO\textsubscript{2} and 1.7% O\textsubscript{2} added to the carbonation gas. 1.7% O\textsubscript{2} was selected to approximate the O\textsubscript{2} concentration in the product gas when methane is burned in 10% excess air. The loss in CO\textsubscript{2} capacity, measured by the loss in dimensionless weight following carbonation, was also about 65% following four cycles.

6.5 Summary

- Five-cycle tests using SBC Grade 3 at standard carbonation and calcination conditions show a gradual loss in both reaction rate ($f(25)$) and final fractional carbonation ($f(150)$) with increasing cycle number.
Figure 6.23 Dimensionless Weight Versus Time Showing the Effect of SO$_2$ in the Carbonation Gas: SBC Grade 3 and 0.1% SO$_2$ with 1.7% O$_2$

- Five-cycle test results using SBC Grade 3 at more severe calcination conditions (160°C in He, 200°C in CO$_2$, and 200°C in 80%CO$_2$/20% H$_2$O) caused the reaction rate to decrease, but capacities were not significantly different, compared to results at less severe standard calcination conditions (120°C in He).

- Five-cycle tests using Trona T-200 at standard calcination and carbonation conditions showed no significant loss of either reactivity or capacity over five cycles.

- More severe calcination conditions (160°C in He and 200°C in CO$_2$) caused decreased reactivities and capacities of Trona samples. In addition, the capacity for Trona decreased more than SBC Grades 3 and 1.

- With the same severe reaction conditions, the order of reactivity and capacity for four sorbents was SBC-1 > SBC-3 > T-50 > T-200.
The formation of increasing amounts of Na$_2$SO$_3$ during each carbonation cycle resulted in decreasing CO$_2$ removal capacity when sorbents were exposed to SO$_2$ concentration as low as 0.1%. In addition, Na$_2$SO$_3$ is stable in He at temperatures as high as 200°C.
Electrobalance tests record the change of sample weight with time, which can be related to fractional solid conversion with time. However, the electrobalance provides no information on CO$_2$ removal efficiency since the gas products are not analyzed. A fixed-bed reactor with the CO$_2$ concentration in the product gas monitored using gas chromatography (GC) has been used to study CO$_2$ removal.

This chapter reports results of the effects of calcination and carbonation temperatures and different sorbents on CO$_2$ removal efficiency and sorbent durability in single-cycle and multi-cycle tests using the fixed-bed reactor. Reaction conditions and sorbents studied were chosen based on the results of electrobalance tests.

7.1 Typical Fixed-Bed Reactor Test

A fixed-bed reactor test using SBC Grade 3 is chosen to describe a typical fixed-bed reactor run. Results are shown in Figure 7.1 in terms of mol percent CO$_2$ in the product gas (dry basis) as a function of time. Approximately 25.1 g of SBC Grade 3 was loaded into the reactor and heated from room temperature to 100°C at a rate of 5°C/min and then from 100°C to the final calcination temperature of 120°C at a rate of 1°C/min under flowing N$_2$. After calcination was complete, which is indicated by no more CO$_2$ being detected in the product gas, the sample was cooled to the desired carbonation temperature of 70°C and left overnight under flowing N$_2$. The next day, an H$_2$O-N$_2$ mixture was fed for 30 minutes to establish H$_2$O vapor flow. Then CO$_2$ was added to form a gas mixture of 8% CO$_2$, 16% H$_2$O and balance N$_2$ at a total flow rate of 300 sccm. Carbonation was continued until the reaction rate approached zero, which was indicated
Figure 7.1 Typical Fixed-Bed Reactor Test: Mol Percent CO$_2$ as a Function of Time During a 1.5 Cycle Test Using SBC Grade 3 with 70$^\circ$C Nominal Carbonation Temperature and a Total Carbonation Feed Rate of 300 sccm.

by constant CO$_2$ composition in the product gas. The CO$_2$ and H$_2$O flows were then stopped and the temperature was increased to 120$^\circ$C for the second calcination. System pressure was 1 atm during calcination and carbonation.

CO$_2$ concentration during the first calcination is shown in the left portion of the figure. The maximum CO$_2$ concentration of 8.4% was reached after about 140 minutes and calcination was complete in about 350 minutes. Numerical integration of the area under the calcination curve showed that 0.155 mols of CO$_2$ were produced compared to a theoretical value of 0.150 mols associated with the 25.1 g initial charge of NaHCO$_3$. The 4% error indicated a good material balance closure.

In the carbonation portion of this test, shown as the middle portion of Figure 7.1, the CO$_2$ concentration-time curve had the general appearance associated with a breakthrough curve. During the first 80 minutes of carbonation the CO$_2$ concentration
was in the range of 4.0% to 4.9% (dry basis), corresponding to CO₂ removal in the range of 50% to 60% based on the theoretical CO₂ feed concentration of 9.5% (dry basis). The CO₂ concentration then gradually increased to a steady-state value of about 10.3% (dry basis), somewhat higher than the 9.5% (dry basis) CO₂ corresponding to zero CO₂ removal. The area above the CO₂ breakthrough curve (to 10.3% CO₂) corresponds to 0.0937 mols of CO₂ removed during carbonation, 62.5% of the theoretical capacity of the Na₂CO₃ based on NaHCO₃ product or 104.2% capacity based on Wegscheider’s salt product. The jagged nature of the CO₂ breakthrough curve may be due to a relatively large MFC error associated with the small CO₂ flow rate, and/or uneven H₂O vaporization.

The right portion of Figure 7.1 corresponds to the second calcination cycle. In this second calcination the maximum CO₂ concentration was 7.2% and the area under the curve corresponded to 0.081 mols of CO₂ released, which is equivalent to 54% theoretical capacity of the Na₂CO₃ based on NaHCO₃ product or 90% capacity based on Wegscheider’s salt product. The 0.081 mols released in the second calcination agrees only approximately with the 0.094 mols of CO₂ removed during carbonation.

7.2 Other Examples of Fixed-Bed Reactor Tests

A syringe pump was used to feed liquid water needed during carbonation in the initial fixed-bed tests. Feed lines were heat traced to produce steam, but the low carbonation temperature made it difficult to vaporize the water and provide just the right amount of preheat energy. With too much preheat energy the combined gas temperature exceeded the desired carbonation temperature; with too little preheat energy vaporization was extremely slow and sometimes incomplete.
In later fixed-bed tests the syringe pump was replaced by a wash bottle. N\textsubscript{2} and CO\textsubscript{2} at the desired flow rates were bubbled through the wash bottle contained in a constant temperature bath at 56°C so that the exit gases would contain the desired steam content of 16% assuming that the product gas reached saturation. Results of one test using the wash bottle to add H\textsubscript{2}O, using SBC-3 and consisting of two calcination and one carbonation cycles with a total carbonation gas feed rate of 300 sccm, are shown in Figure 7.2.

![Figure 7.2 CO\textsubscript{2} Concentration versus Time During a 1.5 Cycle Test Using SBC-3 with 70°C Nominal Carbonation Temperature and a Total Carbonation Feed Rate of 300 sccm Using Bubbler.](image)

The material balance closure was generally good. Complete calcination of the initial SBC-3 charge should produce 0.149 mol of CO\textsubscript{2}, and numerical integration of the area under the CO\textsubscript{2}-time curve corresponds to 0.142 mols of CO\textsubscript{2}. During the initial portion of carbonation the CO\textsubscript{2} concentration (dry basis) was about 6.3%, corresponding to roughly 40% CO\textsubscript{2} removal, for approximately 100 minutes. The CO\textsubscript{2} concentration
then gradually increased to about 9.8% (dry basis). Numerical integration of the area above the CO$_2$ breakthrough curve shows that approximately 0.084 mols of CO$_2$ were removed during carbonation. This value is 56.6% of the theoretical value based on NaHCO$_3$ as the product and 94.4% of the theoretical value based on Wegscheider’s salt product. Finally, the area under the CO$_2$ curve produced during the second calcination corresponds to 0.075 mols, which is just over 10% smaller than the amount removed during carbonation.

The total carbonation feed gas flow rate was decreased to 150 sccm in the subsequent fixed-bed tests to provide longer residence time to promote increased CO$_2$ removal. SBC 3 was used in all 1.5-cycle tests along with standard calcination conditions and standard carbonation feed gas composition. Carbonation temperatures of 60, 70, and 80$^\circ$C were studied. Results of the 1.5 cycle test at carbonation temperature of 70$^\circ$C and carbonation flow rate of 150 sccm are shown in Figure 7.3. The experimental value of CO$_2$ produced during the first calcination, 0.15 mols, was equal to the theoretical value. 0.084 mols of CO$_2$ were removed during carbonation and 0.083 mols of CO$_2$ were liberated during the second calcination period. The problem with this test was the uneven CO$_2$ concentrations measured during the prebreakthrough carbonation period, ranging from about 3.0% to 5.5%. These values correspond to an average of about 50% CO$_2$ removal.

Figure 7.4 shows the results of a 1.5 cycle test using a nominal carbonation temperature of 80$^\circ$C. The same procedure was used in this test except that the sorbent was left overnight as Na$_2$CO$_3$ at the carbonation temperature of 80$^\circ$C, instead of 70$^\circ$C, under flowing N$_2$. The first calcination occurred as expected. The original charge of
Figure 7.3 CO₂ Concentration versus Time Using SBC-3 with 70°C Nominal Carbonation Temperature and a Total Carbonation Feed Rate of 150 sccm.

Figure 7.4 CO₂ Concentration versus Time Using SBC-3 with 80°C Nominal Carbonation Temperature and a Total Carbonation Feed Rate of 150 sccm.

NaHCO₃ was sufficient to liberate 0.152 mols of CO₂ and numerical integration of the area under the calcination curve corresponded to 0.16 mols of CO₂. The striking feature
of Figure 7.4 is that there was essentially no CO$_2$ removal during the carbonation cycle. CO$_2$ concentrations in the product gas were scattered around the 9.5% (dry basis) theoretical level corresponding to no removal, and the second calcination cycle liberated only an extremely small amount of CO$_2$.

Thermodynamic analysis indicated that the maximum temperature for NaHCO$_3$ formation in this gas composition is only slightly above 80°C. In a previous electrobalance test at these conditions, carbonation did occur but at a very low reaction rate. The absence of reaction in the fixed-bed reactor may be attributed to the exothermic nature of the carbonation reaction. A larger temperature increase is expectable in the fixed-bed reactor and only a relatively small temperature rise would be sufficient to prevent carbonation.

The carbonation temperature was decreased to 60°C and results from a 1.5 cycle test are shown in Figure 7.5. The initial calcination occurred as expected with a difference of less than 2% between the theoretical value of 0.152 mols CO$_2$ and the measured CO$_2$ liberated of 0.155 mols. The CO$_2$ concentration during carbonation was initially about 5%, corresponding to about 50% CO$_2$ removal. The concentration then decreased to between 2% and 3% for about 100 minutes after which time the CO$_2$ concentration increased in a standard breakthrough curve. 2% and 3% CO$_2$ in the product gas correspond to about 80% and 70% CO$_2$ removal, respectively. Numerical integration of the area under the second calcination curve corresponds to 0.089 mols CO$_2$ liberated, which is equivalent to almost 60% carbonation based on NaHCO$_3$ product and greater than 95% carbonation based on Wegscheider’s salt product. A large sample-to-sample scatter in CO$_2$ concentration is clearly evident, which is now attributed to mass
flow controller problems. Another mass flow controller was substituted in later tests (see subsequent discussion) and the sample-to-sample scatter decreased significantly.

A second two-cycle test using 60°C carbonation temperature was then carried out to confirm the favorable results in Figure 7.5; these results are presented in Figure 7.6. The measured CO$_2$ liberated of 0.154 mols during the first calcination was only about 3% different from the theoretical value of 0.159 mol. Once again the initial CO$_2$ concentration during carbonation was about 5%. The concentration then decreased to the 2–3% level and numerical integration of the CO$_2$ liberated in the second calcination cycle indicated that 0.081 mols of CO$_2$ were removed. CO$_2$ concentrations as low as 1%, corresponding to about 90% CO$_2$ removal, were measured during the early stages of the second carbonation cycle. This run provided the first indication of improved performance during the second cycle.
Figure 7.6 CO$_2$ Concentration versus Time During a 2-Cycle Test Using SBC-3 with 60°C Nominal Carbonation Temperature and a Total Carbonation Feed Rate of 150 sccm.

It was following this test that the CO$_2$ mass flow controller was changed. This change eliminated a great deal of the sample-to-sample scatter in the CO$_2$ product gas compositions that had plagued earlier fixed-bed tests. The mass flow controller change was made just before beginning the 5.5 cycle tests and the improvement in quality of the product gas analysis is readily apparent in the following figures from these tests.

7.3 Examples of 5.5-Cycle Fixed-Bed Reactor Tests

Results of a 5.5-cycle test using SBC-3 with 60°C carbonation temperature and a total carbonation feed rate of 150 sccm are shown in Figure 7.7. As before, the first calcination was carried out one day with each carbonation and calcination on subsequent days. The sorbent was always left overnight as Na$_2$CO$_3$ at 60°C under N$_2$. The positive effect of the new mass flow controller is immediately evident as the scatter in the CO$_2$ breakthrough curves is greatly reduced.
First cycle calcination material balance closure was good with only a 3.5% difference between measured and theoretical amounts of CO$_2$ liberated. Initial CO$_2$ concentrations were near 1% in all except cycle 1 where the minimum CO$_2$ concentration was about 3%. In addition to the improved performance between cycles 1 and 2, there was no indication of deterioration in performance in subsequent cycles.

These results are indicated more clearly in Figure 7.8 where CO$_2$ concentrations in the carbonation product gas during the five cycles are overlaid. It is obvious that the performance of the first cycle was worse than the subsequent four cycles for the first 170 min, then was slightly better for the next 180 min. The last four cycles were close throughout, but cycle 5 produced slightly lower CO$_2$ concentrations. Finally all five cycles approached almost the same final CO$_2$ concentration.
Figure 7.8 CO$_2$ Concentration versus Time for Five Carbonation Cycles Using SBC-3 with Nominal 60°C Carbonation Temperature and a Total Carbonation Feed Rate of 150 sccm.

Results from the second 5.5-cycle test using a nominal 70°C carbonation temperature are shown in Figure 7.9. The results are qualitatively similar to those of Figure 7.7 except that the minimum CO$_2$ concentration at the beginning of each carbon cycle was larger, and the CO$_2$ removed in each cycle was smaller. Minimum CO$_2$ concentrations were, with the exception of cycle 1, about 3%. In cycle 1 the minimum CO$_2$ concentration was about 5%. Once again, therefore, there is a clear indication of improved performance between cycles 1 and 2, and little, if any, obvious deterioration in performance in subsequent cycles.

Figure 7.10 presents the results from Figure 7.9 more clearly by overlaying the CO$_2$ product gas concentrations for the five carbonation cycles. Similar to the 60°C carbonation results, performance during cycle 1 was worse than in the other cycles for the
Figure 7.9 CO\(_2\) Concentration versus Time for the 5.5-Cycle Test Using SBC-3 with Nominal 70\(^\circ\)C Carbonation Temperature and a Total Carbonation Feed Rate of 150 sccm.

Figure 7.10 CO\(_2\) Concentration versus Time for Five Carbonation Cycles Using SBC-3 with Nominal 70\(^\circ\)C Carbonation Temperature and a Total Carbonation Feed Rate of 150 sccm.
first 150 min, but then became better for the rest of the cycle. The subsequent four cycles were close throughout the entire carbonation period.

Because of its superior performance in electrobalance tests, SBC-1 was also studied in a 5.5-cycle test. All reaction conditions were the same as the previous 5.5-cycle test using SBC-3 and a nominal 60°C carbonation temperature. Results from this test were very close to those shown in Figure 7.7, and the five overlaid carbonation cycle results are presented in Figure 7.11. Again, cycle 1 exhibited the worst performance for the first 200 min, followed by the best performance for the next 200 min. The subsequent four carbonation cycles were quite close, especially in the middle 100 min. Similar to the results using SBC-3 with 60°C carbonation, initial CO₂ concentrations were near 1% in all except cycle 1 where the minimum CO₂ concentration was about 2.5%.

![Figure 7.11 CO₂ Concentration versus Time for Five Carbonation Cycles Using SBC-1 with Nominal 70°C Carbonation Temperature and a Total Carbonation Feed Rate of 150 sccm.](image)
Near the end of all carbonation cycles the measured CO₂ concentration exceeded the theoretical value of 9.5 % (dry basis) corresponding to zero CO₂ removal. The final CO₂ concentrations in the data shown in Figures 7.8, 7.10 and 7.11 ranged from a minimum of 9.4% to a maximum of 10.4%. This problem was also pointed out in 1.5-cycle tests. These high concentrations must indicate either an error in CO₂ or N₂ (or both) flow rates or displacement of previously sorbed CO₂, perhaps by the conversion of NaHCO₃ to hydrate or Wegscheider’s salt.

The performance of SBC Grades 1 and 3 in the 5.5-cycle tests at 60°C and 70°C is further compared in Figures 7.12 and 7.13. Figure 7.12 shows the percent CO₂ removal in the third carbonation sample as a function of cycle number. The third sample was chosen for the comparison because of scatter in results from the first two samples associated with carbonation gas feed rates and composition reaching steady-state values. The improved performance between cycles 1 and 2 with no deterioration in subsequent cycles is clear. The results for SBC Grades 1 and 3 with 60°C carbonation were almost the same. At 60°C the CO₂ removal increased from above 60% in cycle 1 to almost 90% in the remaining cycles for both SBC samples. The comparable numbers for 70°C carbonation were almost 30% in cycle 1 and about 70% in the remaining cycles.

Figure 7.13 shows the final percent conversion of Na₂CO₃ to Wegscheider’s salt product for SBC Grades 1 and 3 during each carbonation cycle as a function of carbonation temperature and cycle number. Overall, the final conversions were quite consistent during all five cycles for all three tests. 60°C carbonation for both SBC samples resulted in about 100% conversion, while percent conversion for carbonation of SBC-3 at 70°C was near 85%.
Figure 7.12 Percent CO₂ Removal as a Function of Carbonation Temperature and Cycle Number Using SBC Grades 1 and 3 (based on CO₂ concentration in the third carbonation sample).

Figure 7.13 Final Percent Conversion to Wegscheider’s Salt as a Function of Carbonation Temperature and Cycle Number Using SBC Grades 1 and 3.
### 7.4 Conclusions

- During 1.5-cycle tests material balance closure was good and prebreakthrough concentrations corresponded to approximately 75% and 50% CO$_2$ removal for carbonation temperatures of 60 and 70°C respectively.

- For SBC-3, the performance at different carbonation temperatures was in the order of 60°C > 70°C > 80°C with almost no CO$_2$ removal at 80°C.

- Results from 5.5-cycle tests show no obvious deterioration with cycle number, as well as improved performance between cycle 1 and the remaining cycles for both SBC Grades 1 and 3 under the reaction conditions. Prebreakthrough CO$_2$ removal increased to approximately 90% and 70% in the remaining cycles at carbonation temperatures of 60 and 70°C respectively.

- Carbonation at 60°C resulted in better performance than at 70°C during the five cycle tests, and there was little difference in performance of SBC-3 and SBC-1 using 60°C carbonation.
Chapter 8
Summary, Conclusions and Recommendations

8.1 Summary

Based on the results of thermodynamic analysis from HSC Chemistry [Roine, 1997] and phase diagrams, an small case electrobalance reactor (thermogravimetric analyzer) and a fixed-bed reactor were used as the primary tools in this research to evaluate the capture of CO\textsubscript{2} from simulated flue gas using sodium-based regenerable sorbents.

Single-cycle electrobalance tests were completed to examine the effects of different sorbent samples, carbonation temperature, carbonation gas composition, and calcination temperature and atmosphere on reaction rate and achievable sorbent capacity. Reproducibility and hydrate formation were also studied. SBC Grade 3 and Trona T-50 were used in most single-cycle tests as representatives of SBC and Trona sorbents.

Multi-cycle electrobalance tests were conducted to test sorbent durability and activity maintenance through several calcination-carbonation cycles. All multi-cycle tests, mostly five cycles, used standard carbonation conditions — 8\% CO\textsubscript{2} / 16\% H\textsubscript{2}O / 76\% He with a total flow rate of 600 sccm at a carbonation temperature of 70^\circ C — while calcination conditions were varied. The effects of calcination temperature and atmosphere, the number of calcination-carbonation cycles, and the presence of contaminants, such as SO\textsubscript{2}, on reaction rate and achievable sorbent capacity were studied. Such information provides preliminary information about the economical viability of this CO\textsubscript{2} capture concept.

Electrobalance tests record the change of sample weight with time, which can be related to fractional solid conversion with time. However, the electrobalance provides no
information on CO₂ removal efficiency since the gas products are not analyzed. A fixed-bed reactor with the CO₂ concentration in the product gas monitored as a function of time using gas chromatography (GC) was used to study CO₂ removal efficiency.

The effects of carbonation temperature and different sorbents on CO₂ removal efficiency and sorbent durability in single-cycle and multi-cycle tests using the fixed-bed reactor were studied. Reaction conditions and sorbents studied were chosen based on the results of electrobalance tests. Calcination conditions of 120°C in flowing N₂ and a carbonation gas composition of 8% CO₂ / 16% H₂O / 76%N₂ were used in all tests. All single-cycle tests used SBC Grade 3 and a total carbonation flow rate of either 300 or 150 sccm with carbonation temperatures from 60 to 80°C. Multi-cycle tests studied both SBC Grades 1 and 3 at a total carbonation flow rate of 150 sccm and carbonation temperatures of 60 and 70°C.

8.2 Conclusions

The phase diagrams and HSC predict the stable carbonation product to be NaHCO₃ at 60°C and 70°C for carbonation conditions of 8% CO₂, 16% H₂O and balance He. Different stable phases at 80°C are predicted. Na₂CO₃•3NaHCO₃ is the predicted solid product using phase diagrams and NaHCO₃ using HSC. X-ray diffraction analysis by Church and Dwight of the carbonation products from a fixed-bed reactor test using SBC-3 at a nominal carbonation temperature of 70°C showed that the products were approximately 85% Wegscheider’s salt (Na₂CO₃•3NaHCO₃) and balance sodium carbonate (Na₂CO₃) [Green, et. al., 2002].

Single-cycle electrobalance tests using SBC samples produced good reproducibility. Reaction rate and final achievable capacity decreased with increasing
carbonation temperature, which agrees with the thermodynamic analysis, while the reaction rate increased with increasing concentration of both CO₂ and H₂O. Single-cycle tests using SBC-3 indicated that calcination temperature and atmosphere had little effect on the subsequent carbonation results. Hydrate formation was favored at lower temperatures and higher H₂O contents in the absence of CO₂. Reproducibility of single-cycle tests using Trona samples was poor and firm conclusions of the effects of temperature and gas composition were not possible. However, SBC Grades 1 and 3 generally had higher capacities than Trona T-50 under the same reaction conditions.

Five-cycle electrobalance tests using SBC-3 at standard carbonation and calcination conditions showed a gradual loss in both reaction rate and final fractional carbonation with increasing cycle number. More severe calcination conditions (160°C in He, 200°C in CO₂, and 200°C in 80%CO₂/20% H₂O) caused the reaction rate to decrease at a faster rate, but capacities were not significantly different compared to results at less severe standard calcination conditions (120°C in He).

Multi-cycle electrobalance tests using Trona T-200 at standard calcination and carbonation conditions showed no significant loss of either reactivity or capacity over five cycles. However, more severe calcination conditions (160°C in He and 200°C in CO₂) caused decreased reactivities and capacities of Trona. The capacities of Trona samples decreased more rapidly than SBC Grades 3 and 1 capacities when calcination conditions became more severe. Under the same reaction conditions, the order of reactivity and capacity for four sorbents was SBC-1 > SBC-3 > T-50 > T-200.

Results from five-cycle electrobalance tests using SBC-3 with a small amount SO₂ (as low as 0.1%) added to the carbonation gas showed that the formation of
increasing amounts of Na$_2$SO$_3$ during each carbonation cycle resulted in a cumulative decrease in CO$_2$ removal capacity. In addition, Na$_2$SO$_3$ is stable in He at temperatures as high as 200°C.

Fixed-bed reactor tests achieved good material balance closure between measured and theoretical values of CO$_2$ liberated. During 1.5-cycle tests using SBC-3 with a total carbonation flow rate of 300 sccm at carbonation temperatures of 60 and 70°C, average prebreakthrough CO$_2$ concentrations corresponded to removals of about 75% and 50%, respectively. In addition, for SBC-3, the performance at different carbonation temperatures was in the order of 60°C > 70°C > 80°C with almost no CO$_2$ removal at 80°C.

5.5-cycle fixed-bed reactor tests showed no obvious deterioration with cycle number, as well as improved performance between cycle 1 and the remaining cycles for both SBC Grades 1 and 3. Prebreakthrough CO$_2$ removal (at the third carbonation sample) increased from 63% and 30% in cycle 1 to approximately 90% and 70% in the remaining cycles at carbonation temperatures of 60 and 70°C, respectively. Moreover carbonation at 60°C resulted in better performance than at 70°C during five cycles, but there was little difference in performance of SBC-3 and SBC-1 under the same reaction conditions.

8.3 Recommendations

Further fixed-bed reactor tests using Trona and other SBC samples need to be conducted to compare with the performance of sorbent precursors. In addition, the effect of more severe calcination conditions on CO$_2$ removal efficiency and sorbent reactivity needs to be studied in the fixed-bed reactor system.
Based on the results from 5.5-cycle fixed-bed reactor tests, a lifetime test should be carried out using the best performing sorbent and reaction conditions in which the highest CO$_2$ removal efficiency and consistent sorbent durability are achieved.
References


Vita

Ms. Ya Liang was born in Chishui, China on December 24, 1975. After finishing her high school in her hometown, she was admitted to Tsinghua University in Beijing, China, and received her bachelor’s degree in chemical engineering in 1999. Then she came to the United States to pursue graduate studies at Louisiana State University, Baton Rouge, Louisiana. She will receive a Master of Science in Chemical Engineering degree in August 2003.

Ms. Liang has various interests in sports, including badminton, basketball, table tennis, jogging and so on. She also likes classical and pop music, dancing, traveling, cooking and making friends.