A Calcium Oxide Sorbent Process for Bulk Separation of Carbon Dioxide

**Annual Report
September 1989 - August 1990**

D.P. Harrison

September 1990

Work Performed Under Contract No.: DE-AC21-89MC26366

For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, West Virginia

By
Louisiana State University
Department of Chemical Engineering
Baton Rouge, Louisiana

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EXECUTIVE SUMMARY

This research effort is designed to investigate the technical feasibility of a high-temperature, high-pressure process for the bulk separation of CO_2 from coal-derived gases. The two-year contract was awarded in September 1989 as a result of solicitation number DE-RA21-89MC26040 entitled "Novel Concepts for Bulk Separation of Gases in Coal Gasification Systems." This report describes the research effort and results obtained during the first year of the effort. The overall project consists of 6 tasks, four of which were active during year 01. Tasks 1 and 2 were completed during the year while activity in Tasks 3 and 6 will carry over into year 02. Tasks 4 and 5 will be initiated during year 02.

Three primary objectives were met in Task 1. A literature search on the calcination-carbonation reactions of CO_2 with calcium-based sorbents was completed. A high temperature, high pressure (HTHP) electrobalance reactor suitable for studying the calcination and carbonation reactions was constructed. This reactor system is now fully operable and we are routinely collecting kinetics data at temperatures in the range of 550-900°C and pressures of 1 to 15 atm. Samples of nine candidate calcium-based sorbents were acquired and tested. These samples were subjected to reaction screening tests as part of Task 2. On the basis of the screening results, three sorbents were selected for more detailed kinetic tests under Task 3.

During the time required to secure components and construct the HTHP reactor, an existing atmospheric pressure electrobalance reactor was used to gain general familiarity with the characteristics of the calcination-carbonation reactions and to obtain comparative kinetic behavior from the nine test sorbents. Six of the test sorbents were

composed primarily of calcium carbonate. One of these samples was chemically pure CaCO_3 (99.97%) while the other five were commercial carbonates obtained from producing quarries. The calcination-carbonation behavior of these samples was found to be qualitatively similar. Complete calcination was easily achieved but the subsequent carbonation reaction effectively stopped at a fractional conversion of approximately 0.8.

The limitation on fractional carbonation could be largely overcome by changing the chemical composition of the calcium oxide precursor. Both chemically pure calcium acetate and a commercial dolomite composed of 54.5% CaCO_3 and 45.0% MgCO_3 (by weight) were completely calcined, and greater than 90% of the calcium was subsequently converted to calcium carbonate. As a result of these screening tests, chemically pure calcium carbonate, chemically pure calcium acetate, and the commercial dolomite were selected for more detailed kinetic testing.

In Task 3, the HTHP electrobalance reactor is being used to study the calcination-carbonation behavior of the three base sorbents as a function of calcination temperature, carbonation temperature, carbonation pressure, and CO_2 concentration. Each test consists of two complete calcination-carbonation cycles to provide kinetics data and to obtain first indications of sorbent performance in multicycle operation. In addition to studying the effects of the primary reaction parameters listed previously, limited tests have been or will be conducted to examine the effect of calcination pressure, calcination gas composition, and background gas composition during carbonation. At this half-way point in the overall project, approximately one-half of the Task 3 tests have been completed.

Tasks 4 and 5 have not yet been initiated. In this effort, one of the three sorbents tested in Task 3 will be selected for more detailed kinetic testing including additional cycles and the effect of typical coal-gas impurities such as H_2S .

Structural property characterization of the sorbents as-received, after calcination, and after carbonation comprise Task 6 activities. Testing to date has concentrated upon pore volume and pore size distribution measurements using mercury porosimetry and BET surface area determination. This work will be extended during year 02 to include helium pycnometry and scanning electron microscopy. In all of the test sorbents, calcination produced an increase in pore volume as the volatile components, primarily CO_2 except in the case of calcium acetate, were driven off. Surface area changes following calcination were less predictable; both increased and decreased surface areas have been measured. Subsequent carbonation of the sorbent causes a decrease in pore volume as CO_2 enters the solid phase. In the case of the pure calcium carbonate sorbent where carbonation stops well short of completion, the pore volume of the final carbonated product is extremely small. For both the calcium acetate and dolomite sorbents where complete carbonation is closely approached, the carbonated product retains appreciable pore volume, thereby providing paths of access for the CO_2 to the interior of the solid.

TASK 1: INTRODUCTION AND PRELIMINARY EFFORT

An important responsibility of the U.S. Department of Energy is the development of new technology which will promote the use of the nation's vast reserves of coal, thereby decreasing our dependence on imported petroleum. Coal gasification technology offers the opportunity for achieving the above objective, while at the same time improving process energy efficiency and reducing the adverse environmental impact associated with present coal utilization processes. Prior DOE research has concentrated upon the development of novel gasification processes, improving existing processes, and in developing technology for the removal of trace impurities present in the coal-derived gas.

The current DOE program seeks to develop novel concepts for the bulk separation of gases from product streams which will provide further improvements in gasification process efficiency and economics. Gas stream components subject to bulk separation include carbon dioxide, carbon monoxide, hydrogen, nitrogen, and methane; separation processes should operate within a temperature range of 100 to 700°C.

This particular project is examining the technical feasibility of a HTHP process for the bulk separation of CO₂ based upon the reversible reaction between CO₂ and CaO.

The ability to achieve HTHP bulk separation of CO₂ may have a positive effect on a number of processes in which coal-derived gas is utilized. These include heating value upgrade, hydrogen production, ammonia or methanol synthesis gas manufacture, and the operating efficiency of molten carbonate fuel cells. In addition, CaCO₃ decomposition may

produce high-purity CO_2 which can be marketed as a refrigerant, for use in fire extinguishers, for beverage carbonation, or for improved petroleum recovery.

The research is limited to a laboratory-scale experimental effort using an electrobalance reactor to identify appropriate ranges of temperature, pressure, and gas composition for both the forward and reverse reactions. A number of CaO-based sorbents having different chemical composition and structural properties are being investigated to define those properties required to achieve both high reactivity and acceptable sorbent durability.

LITERATURE SURVEY

The calcination of limestone for lime production is one of the largest tonnage commercial reactions carried out world-wide. Modern lime kilns operate at atmospheric pressure with temperature in the range of 1200 to 1300°C. This temperature, which is well in excess of the minimum decomposition temperature, is necessary to insure that limestone lumps are completely calcined during their passage through the kiln. The calcination reaction, of course, forms the basis of the sorbent regeneration step in the proposed HTHP CO_2 -separation process. The primary CO_2 removal reaction, which is the reverse of the calcination reaction, is not carried out commercially.

The proposed HTHP CO_2 separation process is based upon a thermodynamic analysis of the reversible reaction. The equilibrium constant, expressed in terms of component activities, may be calculated from the Gibbs free energy by the well-known equation

$$K = \frac{a(\text{CaCO}_3)}{a(\text{CaO}) a(\text{CO}_2)} = \exp(-\Delta G^\circ/RT)$$

If one assumes that pure solid phases are present, $a(\text{CaCO}_3) = a(\text{CaO}) = 1$, and if the gas phase is ideal, $a(\text{CO}_2) = P(\text{CO}_2)$, so that

$$P(\text{CO}_2) = K^{-1} = \exp(\Delta G^\circ/RT).$$

Figure 1 shows calculated values of $P(\text{CO}_2)$ over CaO as a function of temperature using thermochemical data from Hougen et al. (1959). At 650°C, $P(\text{CO}_2) \sim 0.008$ atm. Therefore, at that temperature whenever $P(\text{CO}_2) > 0.008$ atm, the reaction should proceed to the right (carbonation). When $P(\text{CO}_2) < 0.008$ atm, thermodynamics would favor carbonate decomposition. If an entering gas at 650°C and 15 atm contained 15% CO_2 , it is theoretically possible to achieve 99.6% CO_2 removal. With lower temperatures, higher pressures, and/or higher inlet CO_2 mol. fractions, still greater CO_2 removal efficiencies are theoretically possible.

The possibility of using the forward carbonation reaction for CO_2 separation was considered at least as early as the 1920's. Gluud et al. (1931) patented a process for producing hydrogen via a water-gas shift reaction using calcined dolomite. The MgO component of the calcined dolomite was claimed to be responsible for the shift catalysis while CaO reacted with the CO_2 product, thereby continually shifting the reaction to the right and permitting essentially complete removal of carbon oxides from the gas stream, and the production of high-purity hydrogen.

Squires (1967) revived the concept by suggesting the use of dual fluidized-bed reactors to permit steady-state operation and to overcome some of the heat transfer problems associated with Gluud's fixed-bed

Figure 1. Equilibrium CO_2 Pressure as a Function of Temperature.

concept. Squires also proposed the use of calcined dolomite with MgO serving as the shift catalyst and CaO used to react with CO₂. Also in the 1960's, the CO₂ acceptor process (Curran et al., 1967) was studied as a possible means for the simultaneous removal of H₂S and CO₂ from coal-derived gases. Dolomite was used in a fluidized-bed reactor and the sorbent gas was subjected to numerous carbonation-calcination cycles. Each of these studies concentrated upon the process aspects and little or no fundamental kinetics data were reported. Reliable and highly efficient low temperature processes for CO₂ removal were available, and research on the high-temperature process was terminated.

On a more fundamental level, Dedman and Owen (1962) studied the reaction of CO₂ with calcined limestone over the temperature range of 100 to 600°C and the pressure range of 10 to 600 mmHg. The initial reaction was found to be very rapid followed by an abrupt transition to a much slower reaction. The slower second stage was attributed to a process controlled by diffusion of CO₂ in the pores of the solid. An activation energy of 9.5 ± 2 kcal/mol between 200 and 600°C was reported for the diffusion-controlled second stage. It is interesting to note that this is the first instance in which the carbonation reaction was reported to occur in two stages. Such behavior has been regularly reported since.

Two studies by Barker (1973 and 1974) on the CaO-CO₂ reaction provide results which are relevant to the current study. The reaction was studied in an electrobalance reactor at 866°C and 1 atmosphere using calcium carbonate particles in the range of 2 to 20 micron diameter. Figure 2 (from Barker, 1973) shows a typical electrobalance response to numerous calcination-carbonation cycles (curve b). Calcination, which is

Figure 2. Calcination-Carbonation Test Results from Barker (1973).

represented by the weight loss from 100% to 56% [$M(\text{CaCO}_3) = 100$, $M(\text{CaO}) = 56$], was rapid and complete. Carbonation, represented by the weight gain, was initially rapid but the reaction rate dropped off to near zero well short of completion. Calcination was complete in each cycle but the transition from the rapid to the slow reaction rate occurred at progressively smaller values of fractional carbonation with increasing cycle number. The fact that the reaction does not completely stop after the initial rapid rate is shown by curve (a) in which a single carbonation test was extended for 24 hours, at the end of which time the sample weight had increased to approximately 98%.

Such reaction behavior can be explained on the basis of the varying structural characteristics of the reacting solid as the calcination-carbonation reactions progress. Natural limestones commonly possess quite low porosity. However, the calcination reaction creates porosity as CO_2 is driven off. During carbonation the pores are refilled. The refilling process occurs preferentially at the exterior of the particle, and the end of the rapid reaction period is presumed to correspond to total surface pore closure. The remaining unreacted CaO within the particle is carbonated very slowly since CO_2 must diffuse via a solid state or ionic mechanism through the nonporous carbonate layer. Similar problems of pore closure are faced when calcium oxide is used for SO_2 removal in flue gas desulfurization applications.

In his second paper, Barker (1974) used extremely small particles of approximately 20 nm diameter to minimize the quantity of CaO which could be isolated within the particles after pore closure. Calcination was carried out at 629°C and 1 atmosphere in N_2 , and carbonation at 577°C under 1 atmosphere of CO_2 . Approximately 93% carbonation was

achieved during the rapid reaction phase and this value remained essentially constant through 30 complete cycles. While this latter study is of importance in understanding the mechanism of the carbonation reaction, the use of such small particles is not feasible in a commercial process.

Oakeson and Cutler (1979) studied the CaO-CO_2 reaction using an electrobalance over a temperature range of 853 to 1044°C under CO_2 pressures between 2.35 and 24.9 atmospheres. The rate of reaction was reported to follow a parabolic correlation with time, while the pressure dependence was related to a Langmuir-type adsorption isotherm. The reaction was reported to be diffusion controlled with a diffusion activation energy of 29 ± 6 kcal/mol.

Bhatia and Perlmutter (1983) investigated the kinetics of the $\text{CO}_2\text{-CaO}$ reaction using a $\text{CO}_2\text{-N}_2$ mixture at one atmosphere over the temperature range of 400 to 725°C. Their data were analyzed using a random pore model (Bhatia and Perlmutter, 1980 and 1981) and the average value of the rate constant during the initial rapid reaction period was found to be $0.0595 \pm 0.0018 \text{ cm}^4/\text{mol}\cdot\text{s}$. The slow second phase was reported to be diffusion controlled with an activation energy of 88.9 ± 3.6 kJ/mol below 515°C and 179.2 ± 7 kJ/mol above 515°C. 515°C was claimed to be near the Tamman temperature of CaCO_3 (about 533°C), where a change in the solid state diffusion mechanism was said to occur.

Delucia (1985) studied the multicycle behavior of the calcination-carbonation reactions using CO_2 at atmospheric pressure over the temperature range of 50 to 800°C. The carbonation reactivity decreased by 10 to 25% per cycle, which was attributed to continued particle shrinkage during calcination.

Dhupe and Gokarn (1987 and 1990) mixed inert solid with calcium-based sorbent pellets and studied the reaction with CO_2 . Metallurgical grade silicon powders were used as the inert. While they reported a maximum CO_2 uptake capacity at a particular inert concentration, no clear explanation of the results was presented.

Finally, Mess (1989) studied the diffusion process through the CaCO_3 product layer using an electrobalance under CO_2 pressures up to 12 atmospheres at temperatures from 550 to 1050°C. At temperatures of 600°C and above, the product layer contained crystalline grains whose size varied from 1 to 20 microns. The CaCO_3 grains grew laterally and were temperature dependent. Above 900°C, the reaction was first-order in CO_2 pressure and the activation energy in the diffusion controlled region was 56.9 kcal/mol.

A closely related reaction, the sulfation of CaO ,

has been the subject of a great deal of research as a potential method for SO_2 control in flue gas desulfurization applications. One study in particular (Hartman et al., 1978) provides information which is directly applicable to the carbonation reaction. The effect of porosity of the calcium carbonate sorbent precursor on the sulfation reaction was examined. While the initial pore volume of most limestones is low ($\leq 0.05 \text{ cm}^3/\text{g}$), related natural carbonate products such as chalks and marls may have initial pore volumes in the range of 0.1 to 0.2 cm^3/g and 0.25 to 0.9 cm^3/g , respectively (Boynton, 1980).

Hartman et al. (1978) showed that the porosity of the calcined product (CaO) was a strong function of the porosity of the natural rock

(CaCO_3). Figure 3 shows test results which include limestones, chalks, and marls as precursors. The straight lines in the figure are from the equation

$$\epsilon_{\text{CO}} = 1 - \epsilon_{\text{CC}} \left[y \left(\frac{V_{\text{CO}}}{V_{\text{CC}}} - 1 \right) + 1 \right]$$

where ϵ represents porosity, V is the molar volume, and y is the fractional purity. The subscript CC represents the original calcium carbonate starting material and the subscript CO presents the calcined product, calcium oxide. Values of $V_{\text{CO}} = 16.6 \text{ cm}^3/\text{mol}$ and $V_{\text{CC}} = 36.9 \text{ cm}^3/\text{mol}$ were assigned along with values of $y = 0.8, 0.9, \text{ and } 1.0$ to obtain the straight lines. The correlation between measured precursor and product porosities and the geometric arguments represented by the equation is quite good. Calcines from nonporous limestones had porosities in the range of 0.5 to 0.55, while chalks and marls produced calcines having porosities as high as 0.69 and 0.85, respectively.

Subsequent sulfation results shown in Figure 4 (Hartman et al., 1978) illustrate the importance of the calcine porosity on the progress of the sulfation reaction. Using nonporous limestone precursor ($\epsilon_{\text{LS}} = 0$), the fractional sulfation was less than 0.3 after 60 minutes. The moderate porosity chalk ($\epsilon_{\text{LS}} = 0.27$) resulted in 0.6 to 0.7 fractional sulfation after 60 minutes (depending upon particle size), while the calcine from the high porosity marl ($\epsilon_{\text{LS}} = 0.71$) was completely sulfated in approximately 20 minutes.

Finally, in any review of the use of calcium-based sorbents in noncatalytic gas-solid reactions, one would be remiss in not mentioning at least some of the work of Borgwardt. One paper (Borgwardt, 1989)

Figure 3. Porosity of the Calcine as a Function of the Porosity of the Precursor (Hartman et al., 1978).

Figure 4. The Extent of Calcium Oxide Sulfation as a Function of the Porosity of the Precursor (Hartman et al., 1978).

will provide a point of entry which the reader can use to trace back the numerous contributions made by Borgwardt and associates.

The literature provides guidance into the expected behavior of the CaO-CO_2 reaction in several areas. In general, the carbonation reaction is characterized by a rapid initial reaction period followed by an abrupt transition to a slow reaction phase well short of complete calcium conversion. This behavior seems to be related to pore closure at the exterior surface of the particle which prevents CO_2 from reaching unreacted CaO at the interior of the particle. Multicycle tests generally show decreased reactivity with each carbonation cycle, a phenomenon consistent with particle shrinkage and associated reduction in porosity. At least one paper (Bhatia and Perlmutter, 1983) implies that exceeding the Tamman temperature of CaCO_3 could be responsible for the shrinkage.

The literature also suggests possible ways of avoiding or at least delaying the transition from the rapid to the slow reaction phase to obtain increased fractional calcium utilization. Decreasing the sorbent particle size appears to be an effective, but commercially impractical, method. Nanometer diameter particles used by Barker (1974) require special preparation techniques and would be impossible to confine in a commercial process. Increasing the porosity of the sorbent by using a high-porosity precursor such as described by Hartman et al. (1978) seems to be a more promising option. Other options of increasing and/or maintaining porosity during calcination and carbonation include the addition of inerts to the sorbent and using other sorbent precursors.

Although a number of previous studies on the behavior of the CaO-CO_2 reaction have been cited, none provide the broad scope of work

necessary to evaluate fully the feasibility of a CaO-based high-temperature CO₂ removal process. The process patent of Gluud et al. (1971) does not contain any fundamental kinetic data. Similarly, Squires (1967) paper presents a conceptual modification to Gluud's process but again without the necessary kinetic data. Many of the more fundamental studies have examined only a narrow range of conditions such as a single pressure, or a single sorbent, or only a single carbonation cycle. The objectives of the present study are to build upon this past work by studying a number of sorbents having a wide variation in structural properties, to determine the effects of the important reaction parameters over a range of conditions likely to be encountered in a commercial process, and to develop information on sorbent durability through multi-cycle testing. The kinetic data will be supplemented with key structural property measurements of the sorbents at various stages in the reaction cycles.

SORBENT SELECTION

A total of nine calcium-based sorbents have been acquired and subjected to preliminary screening tests (see Task 2). A general description of the sorbents is presented in Table I. Sorbent selection was based upon availability and also upon the desirable properties identified in the literature search. Sample 1, reagent-grade CaCO₃ from Mallinckrodt was selected as the base sorbent against which others would be compared. Samples 2 through 6 were all commercial-grade CaCO₃ obtained from producing quarries. Limestone, chalk, and marl were included in this group in the hopes of matching the type of results shown in Figure 4 by Hartman et al. (1978). Instead, as will be shown,

Table I

Description of Calcium-Based Sorbent Precursors.

Sample No.	General Description	Source
1	Reagent grade calcium carbonate, CaCO_3	Mallinckrodt Chemicals
2	Marl from producing quarry	Gifford-Hill Co. Harleyville, SC
3	Chalk from producing quarry	United Cement Co. Artesia, MS
4	Chalk from producing quarry	Texas Crushed Stone Co. Georgetown, TX
5	Limestone from newly developed quarry in Yucatan, Mexico	Vulcan Materials Co. Houston, TX
6	Chalk from producing quarry	Gifford-Hill Co. Midlothian, TX
7	Reagent grade calcium acetate, $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot x \text{H}_2\text{O}$	Mallinckrodt Chemicals
8	Reagent grade calcium sulfate, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	Mallinckrodt Chemicals
9	Dolomite, $\text{CaCO}_3 \cdot \text{MgCO}_3$	National Lime Co. Findley, OH

Table II Chemical Analysis of Mallinckrodt Analytical
 Reagent CaCO_3 (Sample 1), Chelometric Standard
 (as reported by Mallinckrodt)

CaCO_3	99.97% (after 2 hours at 285°C)
Alkalinity	Passes Test
Ammonium (NH_4)	0.002%
Barium (Ba)	0.002%
Chloride (Cl)	0.001%
Fluoride (F)	0.0009%
Heavy Metals (as Pb)	0.0005%
Insoluble in HCl and NH_4OH ppt	0.00025%
Iron (Fe)	<0.0002%
Magnesium (Mg)	0.0006%
Other Alkalis	Passes Test
Oxidizing Substances (as NO_3)	<0.005%
Potassium (K)	0.0006%
Silica (SiO_2)	<0.0006%
Silicon (Si)	0.0003%
Sodium (Na)	0.002%
Strontium (Sr)	0.006%
Sulfate (SO_4)	<0.0025%

Table III. Chemical Analysis of Mallinckrodt
Analytical Reagent Calcium Acetate (Sample 7)
(as reported by Mallinckrodt)

$\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$	> 91.47%
Barium (Ba)	< 0.005%
Chloride (Cl)	< 0.001%
Heavy Metals (as Pb)	< 0.001%
Iron (Fe)	< 0.001%
Magnesium and Alkali Salts	< 0.2%
Sulfate (SO_4)	< 0.01%
Water	8.3%

the calcination-carbonation behavior of samples 1 through 6 was qualitatively similar.

Sorbents 7 and 8, reagent-grade calcium acetate and reagent-grade calcium sulfate, respectively, were selected in the hope that their decomposition would yield a higher porosity CaO in which the rapid reaction phase would be extended to higher fractional calcium utilization. Finally, sorbent 9, which is a commercial dolomite containing approximately equal molar quantities of MgCO_3 and CaCO_3 , was tested to evaluate the effect of an inert on the carbonation reaction. At reaction conditions, both MgCO_3 and CaCO_3 are calcined to their respective oxides; both components, therefore, are effective in creating porosity during calcination. At carbonation conditions MgO is inert so that pore closure due to CaCO_3 formation should be moderated, and open pores for CO_2 diffusion should remain.

On the basis of the screening tests, three sorbents - samples 1, 7, and 9 - were selected for more detailed testing in Task 3. Chemical analyses of the three selected sorbents are presented in Tables II, III, and IV. More detailed structural property results for these samples are reported subsequently in this report.

HIGH-TEMPERATURE HIGH-PRESSURE ELECTROBALANCE REACTOR

The high-pressure electrobalance reactor system shown schematically in Figure 5 has been constructed and is now being used in the Task 3 test program. The key component of this reactor is a Cahn Model C-100 pressure balance having 100 g capacity and 10 μg sensitivity. The housing and hang-down tube are constructed of 316 stainless steel and the unit is rated for 1500 psig at 600°C. Gases from high-pressure

Table IV

Chemical Analysis of Dolomite (Sample 9)

(as reported by National Lime Co., Findlay, Ohio)

Component	Wt. %
CaCO_3	54.5
MgCO_3	45.0
SiO_2	0.2
Fe_2O_3	0.07
Al_2O_3	0.08
S	0.03
Other	0.12

Loss on ignition after calcination

at 1800°F - 47.4%

Figure 5. Electrobalance Reactor Schematic.

cylinders are fed to the reactor using high pressure mass flow controllers (Porter Instruments Model 201). Water may be added to the feed mixture using a high-pressure syringe pump (Harvard Apparatus Model 909). The gas feed line leading to the side-arm of the hang-down tube is heat traced to induce water vaporization. Inert gas (N_2) which is fed to the balance housing joins with reactive gases (N_2 , CO, CO_2 , H_2 , and H_2O) which enter through the side-arm and the combined gases flow downward over the solid reactant. At typical tests conditions the volumetric flow rate of inert through the balance housing was $300 \text{ cm}^3/\text{min}$ (STP) while the total flow of reactive gases through the reactor side-arm was $200 \text{ cm}^3/\text{min}$ (STP). Exit gases pass first through a condenser and are vented either through a three-way valve for atmospheric pressure tests or through a back-pressure regulator (Tescom Model 26-232-24-0301) for high pressure tests. A similar condenser, three-way valve, back-pressure regulator arrangement is provided in the side-arm gas feed line. Reactive gas flow rate and pressure adjustments are made while directing the gases to vent. Subsequently switching the three-way valve in the side-arm feed line permits reactive gases to be introduced to the reactor with minimum system upset and time delay.

Reactor temperature is maintained using a single-zone split-tube furnace (Applied Test Systems Series 3210) equipped with a single-zone temperature controller which is microprocessor programmable for up to eight ramp and soak intervals. An over-temperature controller provides protection against temperature run-away.

An IBM PS/2 Model 30/286 computer is provided to acquire, store, and process sample weight, reactor temperature, and mass flow controller readings. A data interface package and software supplied by Cahn

Figure 6. Typical Electrobalance Response: One Complete Calcination-Carbonation Cycle.

Instruments are used for data acquisition and processing. Both a printer (Epson RX-100) and plotter (IBM 6/80/001) are provided for hard-copy data output.

A typical electrobalance response curve through one complete calcination-carbonation cycle using reagent grade CaCO_3 (sample 1) is shown in Figure 6. 11.8 mg of CaCO_3 were heated at a rate of approximately $5^\circ\text{C}/\text{min}$ to 750°C under one atmosphere of nitrogen. The high reactor mass produced a nonlinear response during the first 50 minutes of the heating cycle. However, the heating rate approached linearity well before the active reaction temperature was reached.

The sample weight showed a small apparent increase during the early heat-up period prior to the beginning of active calcination. This apparent weight increase was due to increased aerodynamic drag exerted by the flowing nitrogen. Calcination began after 125 minutes at a temperature of approximately 625°C and was complete after 150 minutes, coinciding approximately with the time that the temperature reached the final 750°C set-point. The sample weight of 6.6 mg at the end of calcination corresponds to the theoretical weight associated with the complete decomposition of pure CaCO_3 to CaO . After 160 minutes, the reactor pressure was increased to 5 atmospheres of nitrogen. At the same time, the pressure and flow rate of N_2 and CO_2 in the side-arm were adjusted and directed to vent. No CO , H_2 , or H_2O was present in the feed gas for this run.

As shown in Figure 6, system pressurization produced a great deal of temporary upset in the sample weight reading. Once the final pressure of 5 atmospheres was reached, the sample weight also stabilized. After 210 minutes, the three-way valve in the side-arm was

switched and reactive gas composed of 15% CO_2 , balance N_2 was directed over the sample. The carbonation reaction began immediately as evidenced by the solid weight increase to approximately 10.3 mg within two minutes. Thereafter, the rate was quite slow and a maximum weight of 10.9 mg was reached when the run was terminated after 280 minutes. The 10.3 and 10.9 mg weights correspond to fractional carbonations of 0.71 and 0.83, respectively. These typical results are, therefore, consistent with previous results reported in the literature.

TASK 2: REACTION SCREENING TESTS

A number of calcination-carbonation screening tests were carried out as part of Task 2 activities in order to determine the general characteristics of the reactions as a function of temperature, pressure, and gas composition as well as to compare the reactivity of the various sorbents (see Table I). As a result of these screening tests, three sorbents have been selected for more detailed kinetic testing under Task 3, and the ranges of parameters to be studied in Task 3 have been defined.

Most of the tests were conducted using an existing atmospheric pressure electrobalance reactor system while the high pressure reactor was being constructed. The principle behind the two reactors is identical. Important practical differences between the two, in addition to the pressure limit, are as follows. Gas flow rates in the atmospheric pressure reactor were controlled manually using rotameters and needle valves instead of mass flow controllers. The reduced thermal mass of the atmospheric pressure reactor permitted much faster temperature response. For example, rates of temperature change of 50°C/min were easily achieved in the low pressure reactor while approximately 5°C/min has been found to be the maximum practical value in the high pressure unit. In the low pressure unit, the experimental data (sample weight and temperature as a function of time) were acquired and stored using an electronic recorder (Bascom-Turner) rather than the PS-2 computer system used in the high pressure unit. In addition, it appears that, at approximately 750°C, the temperature in the low pressure reactor was 20 to 30°C lower than the set-point. This caused no problems in comparing results between low pressure reactor runs, but

caution must be exercised in comparing runs at "identical" conditions from the low and high pressure reactors.

CHARACTERISTICS OF THE CALCINATION-CARBONATION REACTIONS

A number of tests in Task 2 were carried out to learn more about the general characteristics of the calcination-carbonation reaction. Most of the tests used sample 1 (reagent calcium carbonate) and most were performed using the atmospheric pressure reactor. The results of these tests were used to establish the ranges of the reaction parameters to be studied in Task 3.

THE EFFECT OF TEMPERATURE

Figure 7 shows the effect of temperature on the calcination rate. Calcination was carried out in nitrogen at 1 atmosphere using a heating rate of 50°C/min to the indicated temperature, with isothermal operation thereafter. Calcination began at a very low rate at approximately 600°C, and the rate increased rapidly with temperature to 845°C. Calcination was complete within the 50 minute time frame shown in the figure at both 745 and 845°C. Longer time data (not shown) suggests that calcination would be complete at 660°C after approximately 200 minutes and after about 65 minutes at 710°C.

The effect of carbonation temperature is shown in Figure 8 using a calcination temperature of 750°C. Carbonation was carried out at 1 atmosphere in 5.6% CO₂, balance N₂. Each test resulted in an initial rapid reaction period followed by an abrupt change to a slow reaction phase. This behavior is in general agreement with previous results reported in the literature. Both the time and extent of carbonation at the end of the rapid phase are strong functions of temperature. The

Figure 7. The Effect of Temperature on Calcination Kinetics:
Sample 1.

Figure 8. The Effect of Temperature on Carbonation Kinetics:
Sample 1.

final values of W/W_0 , which ranged from approximately 0.63 at 430°C to 0.89 at 750°C, correspond to fractional carbonations of approximately 0.16 to 0.75, respectively. The global rate during the rapid reaction phase was approximately equal in the temperature range from 430 to 680°C; the decrease in the global reaction rate at 750°C is attributed to the fact that the actual partial pressure of CO_2 was only slightly greater than the equilibrium partial pressure at this temperature.

Although each test exhibited a similar sharp decrease in global rate after a certain time, the carbonation reaction never stopped completely as shown in Figure 9. In this test, calcination at 895°C in N_2 at 1 atmosphere was followed by carbonation at 710°C in 15% CO_2 , balance N_2 , with the carbonation cycle extended to 24 hours. The rapid reaction period, which lasted for approximately 5 minutes, appears to end instantaneously at $W/W_0 = 0.85$, corresponding to X (fractional carbonation) ~ 0.66 . Over the next 24 hours, W/W_0 gradually increased to 0.93, corresponding to $X \sim 0.84$.

THE EFFECT OF GAS COMPOSITION

The most interesting and unexpected result from the reaction screening tests concerned the effect of gas composition on carbonation kinetics. The carbonation rate should certainly be dependent upon the CO_2 concentration. This is confirmed by the results in Figure 10. The time scale in this figure is enlarged to emphasize the early reaction period. All calcination conditions and carbonation temperature were equal in each run. While higher CO_2 concentration produced a marked increase in rate during the rapid reaction period, there was relatively little difference in the carbonation level at the end of the test.

Figure 9. Long-Term Carbonation Results: Sample 1.

Figure 10. The Effect of CO₂ Composition on Carbonation Kinetics: Sample 1.

In all carbonation tests discussed to this point, the reactive atmosphere consisted of CO_2 and N_2 only. The following discussion reports the results of tests in which other components were added, in a stepwise manner, to produce a simulated coal gas containing CO , CO_2 , H_2 , H_2O and N_2 . Sample 1 (reagent calcium carbonate) was the sorbent in each case.

Figure 11 compares carbonation results from the CO_2/N_2 atmosphere to results obtained in an atmosphere containing $\text{CO}_2/\text{CO}/\text{H}_2/\text{N}_2$ (at the same CO_2 concentration). The latter atmosphere contains all of the major components present in coal-gas except steam. Addition of CO and H_2 appears to result in a decrease in rate during the rapid reaction period; however, the decrease is slight and could be the result of normal data scatter. In each case the rapid reaction period ends at essentially the same level of W/W_0 .

The more complex gas composition lies in the equilibrium carbon deposition region (Lamoreaux et al., 1986), and, after the test, carbon deposits were noted on the walls of the hang-down tube downstream of the sorbent. Carbon deposition on either the sorbent or the hang-down wire or pan would produce a weight gain, thereby confounding the carbonation kinetics. In order to check for carbon deposition, two blank runs were made in which inert Al_2O_3 was substituted for reactive CaO . Two gas atmospheres, that shown in Figure 11, and a similar gas with H_2O added, were tested. Addition of H_2O left the gas composition within the carbon deposition region, but nearer the boundary, thereby reducing somewhat the carbon deposition tendency. However, no weight gain was observed with either test showing that carbon deposition does not occur on the critical components to an extent sufficient to confound the carbonation results.

Figure 11. The Effect of Gas Composition on Carbonation Kinetics, The Addition of CO and H₂: Sample 1.

The addition of steam to complete the simulated coal-gas atmosphere produced a dramatic increase in the carbonation rate during the rapid reaction phase as shown in Figure 12. Once again there was no apparent change in the final fractional carbonation. Two possible reasons for the rate increase were considered. Since all components involved in the water-gas shift reaction were present, the occurrence of this reaction would increase the CO_2 concentration above that of the feed gas, and cause the rate in the rapid reaction phase to increase. Secondly, it was considered possible that H_2O simply served as a rate enhancer.

Results of an additional test tests designed to evaluate the possible importance of the shift reaction are shown in Figure 13. In one test, the "simple" gas composed of 5% CO_2 in N_2 was used. In the second, a simulated coal gas containing 5% CO_2 and the indicated amounts of CO , H_2 , H_2O and N_2 was fed. A marked increase in rate during the rapid reaction period with no change in the final value of W/W_0 was observed. The third test gas was composed of 8.9% CO_2 in N_2 , and the rate was similar to that observed in the simulated coal gas. Shift equilibrium calculations showed that if the simulated coal gas feed was allowed to equilibrate, the CO_2 composition would be increased to approximately 9%. While the evidence is indirect, the similarity in the two rate curves suggests that the carbonation and water-gas shift reactions may occur simultaneously when the necessary shift components are present.

Other evidence of the probable importance of the shift reaction is shown in Figure 14. In this test, the CO_2 feed concentration was held constant while the background gas composition was changed ten minutes into the run. During the early stages when the feed gas consisted of 5% CO_2 /27% H_2 /68% N_2 , no carbonation occurred. Reverse shift equilibrium under these feed conditions would leave approximately 1% CO_2 in the gas,

Figure 12. The Effect of Gas Composition on Carbonation Kinetics, The Addition of CO, H₂O, and H₂: Sample 1.

Figure 13. Testing for the Presence of the Shift Reaction:
Sample 1.

Figure 14. Carbonation Kinetics With Constant CO₂ Concentration and Varying Background Gas Composition: Sample 1.

which, at 1 atmosphere and 750°C is below the equilibrium CO_2 pressure for the carbonation reaction. After 10 minutes, H_2 feed was stopped and H_2O was added to stop the shift reaction from occurring. As indicated in the figure, carbonation began immediately, and proceeded to a W/W_0 value approximately equal to that observed in the simple CO_2/N_2 composition.

Results of one final test showing the importance of background gas composition are shown in Figure 15. In this test, the feed gas contained no CO_2 but did contain the shift reactants CO and H_2O . The observed weight increases proves that carbonation did occur, and the only reasonable source of CO_2 was the shift reaction. The fact that the W/W_0 value reached a maximum of approximately 0.68 after 10 minutes and declined thereafter suggests that CO_2 formation was transitory. This behavior would be consistent with CaO serving as a shift catalyst. Early in the test when most of the sorbent was in the oxide form, the shift reaction produced CO_2 which subsequently reacted to form CaCO_3 . Once an appreciable quantity of CaCO_3 was formed, the catalytic effect diminished, less CO_2 was formed, and a portion of the CaCO_3 decomposed.

The possibility of simultaneous shift reaction - CO_2 removal provides a number of interesting options in so far as a one-step process for the production of hydrogen is concerned. While such options should be pursued, they are beyond the scope of the present study. The combined reactions create problems for the current study in that the CO_2 concentration in contact with the CaO sorbent is no longer determined by the feed gas composition whenever shift reaction components are present. For this reason, a decision was made to concentrate in the Task 3 kinetic studies on the "simple" reactive gas containing only CO_2 and N_2 .

Figure 15. Carbonation With No CO₂ in the Feed Gas: Sample 1.

with a few tests added to provide further information of the effect of background gas composition.

COMPARISON OF SORBENT REACTIVITY

Calcination results for the six calcium carbonate test sorbents (samples 1-6) are compared in Figures 16 and 17. Calcination conditions were equivalent in each test and results from sample 1 are included in both figures for reference purposes. All calcination results were qualitatively similar. The calcination rate became appreciable after about 12 minutes with $T \sim 625^{\circ}\text{C}$. Complete calcination, as evidenced by the constant values of W/W_0 occurred in the range of 43 to 75 minutes. We attribute the differences in time for complete calcination primarily to particle size effects among the samples. Differences in the values of W/W_0 at complete calcination were due to differences in impurity levels. The final weight of sample 1, which was pure CaCO_3 , was quite close to the theoretical value of 0.56. The final value of W/W_0 for the other samples, all of which were obtained from commercial quarries, ranged from 0.56 to 0.64.

Comparable carbonation curves for these samples are shown in Figures 18 and 19. Again, data for sample 1 is included in both figures for reference purposes. In Figure 18 carbonation was carried out isothermally at 630°C while 750°C carbonation temperature was used in the Figure 19 tests. The carbonation gas in all tests consisted of 5.6% CO_2 in N_2 . Differences in the initial values of W/W_0 reflect the differences in the final W/W_0 values from the calcination cycle. Within limits, each of the carbonation curves are similar. In particular, the final values of W/W_0 at the end of the test ranged from 0.82 to 0.85 at 630°C (Figure 18), while the final W/W_0 values from the three 750°C

Figure 16. Comparison of Calcination Kinetics: Samples 1, 2, 4 and 5.

Figure 17. Comparison of Calcination Kinetics: Samples 1, 3, and 6.

Figure 18. Comparison of Carbonation Kinetics: Samples 1, 2, 4, and 5.

Figure 19. Comparison of Carbonation Kinetics: Samples 1, 3, and 6.

tests (Figure 19) were all approximately 0.89. These results were somewhat disappointing. Instead of chalks and marls providing significantly increased reactivity as reported by Hartman et al. (1978) in their sulfation studies, the carbonation behavior of all samples was similar to that of the reagent grade CaCO_3 .

An alternate approach to increasing sorbent reactivity was then pursued. Samples 7 and 8, consisting of reagent grades of calcium acetate and calcium sulfate, respectively, were chosen as test sorbent precursors. The rationale in these selections was that decomposition of either precursor would involve driving off a significantly increased quantity of volatile material leaving CaO with increased pore volume and, presumably, greater carbonation reactivity.

Figure 20 shows decomposition-carbonation results for one complete cycle using sample 7 (calcium acetate). The precursor, $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot x\text{H}_2\text{O}$ containing 8.3% H_2O , was heated in N_2 as shown. Water of hydration was driven off in two increments in the temperature range 100-300°C, leaving $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$ with $W/W_0 \sim 0.92$. Acetate decomposition began at about 450°C and a constant weight plateau was reached at 600°C with $W/W_0 \sim 0.58$. This value of W/W_0 corresponds to that expected for CaCO_3 formed from the original acetate. Additional weight loss to $W/W_0 = 0.314$ occurred in the vicinity of 750°C. No further weight loss occurred during 45 minutes in N_2 at 750°C, and the final weight corresponded closely to the theoretical value of $W/W_0 = 0.325$ for the production of CaO from calcium acetate containing 8.3% H_2O . Carbonation was initiated after 105 minutes by exposing the sorbent to 5.6% CO_2 in N_2 . Weight gain was rapid and the final value of $W/W_0 = 0.57$ corresponded closely to the value expected for total conversion of CaO to CaCO_3 ($W/W_0 = 0.58$).

Figure 20. Decomposition-Carbonation Kinetics: Sample 7.

Hydrated calcium sulfate, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (sample 8) was also examined as a possible precursor with results shown in Figure 21. The atmosphere during CaSO_4 decomposition was 50% N_2 -50% H_2 , with the hydrogen added to promote the removal of sulfur as H_2S . Past work in this laboratory (Focht et al., 1989) showed that when ZnSO_4 was exposed to a reducing atmosphere at high temperature, ZnO was produced as the solid product. Water of hydration was lost in the temperature range of 150-350°C to produce anhydrous CaSO_4 with $W/W_0 = 0.79$. Further weight loss to $W/W_0 = 0.42$ occurred in the temperature range 800 to 1000°C. However, this final $W/W_0 = 0.42$ corresponded to CaS formation instead of CaO ($W/W_0 = 0.33$). At 110 minutes hydrogen was purged from the system and the temperature was decreased to 750°C; when 5.6% CO_2 was added at 130 minutes, essentially no weight gain occurred, thus providing additional evidence that the decomposition product was CaS instead of CaO . Overall, the attempt to increase the carbonation reactivity by decomposing calcium compounds to produce CaO having greater porosity was half successful and half a total failure. As a result, calcium acetate (sample 7) was selected as the second base sorbent to be tested in Task 3.

Sample 9 was a commercial dolomite containing approximately equal molar quantities of CaCO_3 and MgCO_3 obtained from National Lime Co. Dolomite was chosen in order to test the possible diluent effect of magnesium. Calcination of both calcium and magnesium carbonates should be effective in producing porosity in the product mixed oxides. Subsequent carbonation of CaO would reduce porosity as before. However, at carbonation conditions of interest, MgO does not carbonate, but should act as a diluent to modify the degree of pore closure experienced by pure CaO . Results for one complete calcination-carbonation cycle

Figure 21. Decomposition-Carbonation Kinetics: Sample 8.

using the high pressure reactor are shown in Figure 22. Calcination began at approximately 450°C and was complete at about the time the sample reached the desired final temperature of 750°C. Calcination of MgCO_3 should occur at lower temperature, followed by calcination of CaCO_3 . Experimentally, however, calcination began at a lower temperature compared to pure CaCO_3 , but there was no clearcut distinction in the weight loss curve between MgCO_3 and CaCO_3 . The final value of W/W_0 corresponded closely to the loss on ignition value reported by National Lime, and represented complete conversion of CaCO_3 and MgCO_3 to the respective oxides.

Carbonation was carried out at 750°C, 1 atm, in 15% CO_2 (balance N_2), conditions where CaO can be carbonated but not MgO . Carbonation behavior was qualitatively similar to that exhibited by other sorbents. A rapid initial reaction period lasting less than 5 minutes was followed by an abrupt transition to a slow reaction phase. The transition, however, occurred at $W/W_0 \sim 0.73$, which corresponds to a fractional calcium carbonation of 0.85, significantly higher than observed using pure CaCO_3 . 60 minutes after the beginning of carbonation the value of W/W_0 was 0.75, which corresponds to 0.93 fractional calcium carbonation. Because of the favorable results, dolomite (sample 9) was chosen as the third base sorbent for Task 3 testing.

Figure 23 provides a direct comparison of first-cycle carbonation behavior for the three base sorbents at equivalent carbonation conditions. Fractional carbonation, X , is reported on the y-axis instead of W/W_0 as used previously to facilitate the direct comparison between different samples. While each sample exhibits qualitatively similar behavior, it is clear that, at these conditions, greater than 90% carbonation can be achieved using samples 7 and 9, compared to only about 80% carbonation for sample 1.

Figure 22. Calcination-Carbonation Kinetics: Sample 9.

Figure 23. Comparison of First Cycle Carbonation Kinetics: Samples 1, 7, and 9.

TASK 3: TWO-CYCLE TEST SERIES

The objective of Task 3 was to test the calcination-carbonation kinetics of the three base sorbents as a function of temperature, pressure, and gas composition. Each test consisted of two complete calcination-carbonation cycles so that preliminary information on sorbent durability would also be obtained. Reaction conditions were chosen on the basis of results from the screening program in Task 2.

The primary parameters to be tested and their values are:

- a. Calcination Temperature (3): 750, 825, 900°C
- b. Carbonation Temperature (3): 550, 650, 750°C
- c. Carbonation Pressure (3): 1, 5, 15 atm
- d. CO₂ Mol Fraction (3): 0.01, 0.05, 0.15

The complete matrix defined above consists of 243 tests (3 sorbents x 3 calcination temperatures x 3 carbonation temperatures x 3 carbonation pressures x 3 CO₂ mol fractions). Because this number of tests is unrealistic, deletions from the test matrix are being made as results are generated. Additional "off-matrix" tests involving secondary variables such as calcination gas composition, calcination pressure, and carbonation background gas composition will be carried out as need arises and as time permits.

The status of the Task 3 test matrix through August 1990 is shown in Tables V, VI, and VII for samples 1, 7, and 9, respectively. Completed tests are designated by the run number, HPXXX, in the appropriate row and column. As a normal rule only a single test has been carried out at a given set of test conditions. Reproducibility tests have been and will continue to be made periodically; tests which have been reproduced are designated by the multiple run number entries in a single position.

Table V

Task 3 Test Matrix for Calcium Carbonate (Sample 1)

CALCINATION TEMP C	CARBON- ATION TEMP C	CARBON- ATION ATM% CO ₂	CARBONATION PRESSURE 1 ATM	CARBONATION PRESSURE 5 ATM	CARBONATION PRESSURE 15 ATM
900	750	15	HP048		HP040
900	750	5			
900	750	1			
900	650	15			
900	650	5			
900	650	1			
900	550	15			
900	550	5			
900	550	1			
825	750	15	HP047		HP039
825	750	5			
825	750	1			
825	650	15	HP045		
825	650	5	HP051		
825	650	1			
825	550	15			
825	550	5			
825	550	1			
750	750	15	HP021;023;066	HP063	HP032
750	750	5			HP034
750	750	1			HP033
750	650	15	HP046		
750	650	5	HP043		
750	650	1			
750	550	15	HP049		
750	550	5			
750	550	1	HP050;059		

Table VI

Task 3 Text Matrix For Calcium Acetate (Sample 7)

CALCINATION TEMP C	CARBON- ATION TEMP C	CARBON- ATION ATM% CO ₂	CARBONATION PRESSURE 1 ATM	CARBONATION PRESSURE 5 ATM	CARBONATION PRESSURE 15 ATM
900	750	15	HP055		HP076
900	750	5			
900	750	1			
900	650	15			
900	650	5			
900	650	1			
900	550	15			
900	550	5			
900	550	1			
825	750	15	HP053		
825	750	5			
825	750	1			
825	650	15	HP054		
825	650	5	HP052		
825	650	1			
825	550	15			
825	550	5			
825	550	1			
750	750	15	HP022;025;067; 068	HP064	HP036
750	750	5			HP037
750	750	1			HP038
750	650	15	HP056		
750	650	5			
750	650	1			
750	550	15	HP061		
750	550	5			
750	550	1	HP060		

Table VII

Task 3 Test Matrix for Dolomite (Sample 9)

CALCINATION TEMP C	CARBON- ATION TEMP C	CARBON- ATION ATM% CO ₂	CARBONATION PRESSURE 1 ATM	CARBONATION PRESSURE 5 ATM	CARBONATION PRESSURE 15 ATM
900	750	15	HP062	//////////	HP077
900	750	5		//////////	
900	750	1			
900	650	15		//////////	
900	650	5		//////////	
900	650	1		//////////	
900	550	15		//////////	
900	550	5		//////////	
900	550	1		//////////	
825	750	15	HP078		
825	750	5			
825	750	1			
825	650	15			
825	650	5			
825	650	1			
825	550	15			
825	550	5			
825	550	1			
750	750	15	HP057	HP069	HP075
750	750	5			
750	750	1			HP080
750	650	15	HP071		
750	650	5	HP072		
750	650	1			
750	550	15	HP073		
750	550	5	HP074		
750	550	1			

Tests which have been eliminated are designated by the rows and columns marked with the vertical and slanted lines. Eliminations have so far been based upon two criteria: (1) equilibrium constraints and (2) the apparent adverse effect of the highest calcination temperature on carbonation kinetics. Examination of Figure 1 shows that the equilibrium CO_2 partial pressure at 750 and 650°C are approximately 0.07 and 0.007 atmospheres, respectively. Consequently, 36 tests at 650 and 750°C carbonation temperature in which the CO_2 partial pressure was below or quite near the equilibrium limit were eliminated (vertical lines). An additional 21 tests involving 900°C calcination temperature have been eliminated based upon the perceived adverse effect of this calcination temperature on subsequent carbonation kinetics (slanted lines). In total, runs at 39 test conditions have been completed while 57 test conditions have been eliminated, leaving 147 openings in the test matrix.

Reaction Reproducibility

Reproducibility tests are important to establish a baseline expectation of normal run-to-run variation so that the effects of reaction parameter changes may be evaluated. Figure 24 compares the W/W_0 versus time behavior for runs HP067 and HP068 using sample 7. Reproducibility is quite good in this and other tests leading to the conclusion that relatively minor changes in reactivity in response to reaction parameter changes are significant.

The Effect of Calcination Temperature

As shown in the previous section, calcination in a CO_2 -free atmosphere is complete by the time the temperature reaches 750°C.

Figure 24. Reaction Reproducibility: Runs HP067 and HP068 Using Sample 7.

Consequently, the objective of the study of calcination temperature is to determine any effect on the subsequent carbonation kinetics. Three calcination temperatures of 750, 825, and 900°C have been studied. Figures 25 and 26 show the fractional carbonation-time data for the first and second carbonation cycles, respectively, for sample 9 as a function of calcination temperature. Carbonation conditions were identical in each test. Figure 25 shows a relatively minor decrease in the carbonation rate with increasing calcination temperature during the rapid reaction phase. The final conversion (after 60 minutes) was also slightly lower following 900°C calcination. Second-cycle results (Figure 26) are similar but the negative effect of calcination temperature is magnified. There is a clear reduction in both the rate during the rapid reaction period and the final fractional carbonation. The graphical results are reinforced by the following numbers which report $X(60)$, the fractional carbonation after 60 minutes, for each calcination temperature for the first- and second-cycles:

Calcination Temp., °C		750	825	900
$X(60)$	First-Cycle	0.93	0.95	0.92
	Second-Cycle	0.94	0.92	0.86

The apparent small increase in second-cycle conversion following 750°C calcination is probably not significant; however, the decrease following 900°C calcination is believed to be significant. Similar negative effects of high calcination temperature have been noted with the other base sorbents as well.

These results led to the decision to eliminate numerous 900°C calcination runs from the test matrix. While other tests involving 900°C calcination will probably be eliminated in the future, some

Figure 25. The Effect of Calcination Temperature on First-Cycle Carbonation Kinetics: Sample 9.

Figure 26. The Effect of Calcination Temperature on Second-Cycle Carbonation Kinetics: Sample 9.

additional runs are planned to confirm that the present conclusions are not premature.

The Effect of Carbonation Temperature

Quite interesting and unexpected results concerning the effect of carbonation temperature, particularly on second-cycle kinetics, have emerged from the tests completed to date. Figure 27 shows the first-cycle carbonation results for a series of tests at different carbonation temperatures using sorbent sample 1. Carbonation was preceded by calcination at the minimum temperature of 750°C. The results are generally consistent with the previously reported screening results on the effect of carbonation temperature (Figure 8). Both the duration of the rapid reaction phase and the fractional carbonation at the end of the rapid reaction phase increased with increasing temperature. The rate during the rapid reaction phase showed little effect of temperature at 550 and 650°C, but a large decrease in rate was observed at 750°C. This decrease is attributed to the increasing importance of the equilibrium CO_2 pressure at the highest temperature.

The surprising result concerns a large drop in second-cycle carbonation activity associated with 550°C carbonation temperature. A typical example is shown in Figure 28 where first- and second-cycle carbonation data for a sample 7 test are shown. After 20 minutes the fractional carbonation in cycle two was 20% less than observed in the same time in cycle one. In contrast, second-cycle conversions at the higher carbonation temperatures of 650 and 750°C were much closer to the first-cycle results. The adverse effect at 550°C seems to be common to each of the three sorbents as shown by the data in Table VIII. In this table, the fractional carbonation after twenty minutes in the first and

Figure 27. The Effect of Carbonation Temperature on Carbonation Kinetics: Sample 1.

Figure 28. Comparison of First- and Second-Cycle Carbonation Kinetics at 550°C: Sample 7.

Table VIII: Comparison of First and Second Cycle Fractional Carbonations After Twenty Minutes as a Function of Temperature.

Carbonation Temp., °C	550	650	750
Sample 1, Run	HPO49	HPO46	HPO66
X_1 (20)	0.66	0.72	0.77
X_2 (20)	0.52	0.58	0.66
X_2 (20)/ X_1 (20)	0.79	0.81	0.86
Sample 7, Run	HPO61	HPO56	HPO67
X_1 (20)	0.88	0.90	0.92
X_2 (20)	0.69	0.90	0.92
X_2 (20)/ X_1 (20)	0.78	1.00	1.00
Sample 9, Run	HPO73	HPO71	HPO57
X_1 (20)	0.89	0.94	0.92
X_2 (20)	0.71	0.94	0.88
X_2 (20)/ X_1 (20)	0.80	1.00	0.96

Calcination at 750°C, 1 atm, N_2
 Carbonation at 1 atm, 15% CO_2

second cycles, $X_1(20)$ and $X_2(20)$, and the ratio of these values for each sorbent at each carbonation temperature are presented. Both samples 7 and 9 show good reactivity maintenance [$X_2(20)/X_1(20) \geq 0.96$] at 650 and 750°C carbonation temperatures, but a significant fall-off at 550°C. The reactivity maintenance of sample 1 is much lower than the other samples at 650 and 750°C, and falls off to a lesser degree at 550°C. All three samples exhibit approximately equal reactivity maintenance at 550°C. At the present time, we have no explanation for this unexpected behavior.

The Effect of CO₂ Composition

Tests in which the CO₂ concentration (mol fraction) was varied produced no unusual or unexpected results. Figure 29 compares the first cycle carbonation kinetics for sample 1 with calcination carried out at 750°C and 1 atmosphere in N₂ and carbonation carried out at 750°C and 15 atmospheres using CO₂ mol fractions of 0.01, 0.05, and 0.15. As expected, the rate during the initial rapid rate period increased with increasing CO₂ concentration. The final value of W/W_0 was effectively the same in each case. Second-cycle results for these tests were similar except for the fact that the final value of W/W_0 (after 40 minutes) was approximately 0.84 compared to 0.90 in the first cycle. This level of reduction in the extent of carbonation during the second cycle is consistent with other results for sample 1 at other reaction conditions (see Table VIII). The equivalent test series using sample 7 (calcium acetate) produced similar results except for the fact that the drop-off in reactivity during the second carbonation cycle was less severe.

Figure 29. The Effect of CO₂ Composition on First-Cycle Carbonation Kinetics: Sample 1.

The delay from $t = 0$, when the three-way valve in the gas feed line was switched, and the beginning of the rapid reaction phase is particularly apparent in the 15 atmosphere data presented in Figure 29. Approximately 5 minutes elapsed before the reaction began with the 1% CO_2 test, while the delays at the higher concentrations were approximately 1.5 and 2 minutes. This delay is associated with the time required for the reactive gas to reach the sample after the side-arm valve is opened. The delay time increases with system pressure because of the reduced volumetric flow rate and also increases with decreasing CO_2 concentration. At 1 atmosphere the delay is hardly noticeable, as seen in the previous figures reporting low pressure test results.

The Effect of Pressure

At constant mol fraction of CO_2 , an increase in the system pressure may produce two counteracting effects. Since CO_2 concentration is directly proportional to pressure, an increase in the rate during the rapid reaction phase similar to that shown in Figure 29 should result. However, if transport resistances are important in determining the global rate, an opposing effect is introduced since both mass transfer and pore diffusion coefficients decrease with increasing pressure. The net effect, therefore, of an increase in system pressure could even be a decrease in global rate.

The effect of reactor pressure at constant CO_2 mol fraction is illustrated in Figure 30 for sample 9. Although the varying time delay with pressure complicates the data somewhat, there is a clear increase in the rapid reaction rate between 1 and 5 atmospheres. However, the rates during the rapid reaction phase are approximately equal at 5 and 15 atmosphere. This latter observation suggests that the opposing

Figure 30. The Effect of Pressure at Constant CO₂ Mol Fraction: Sample 9.

effects of increased concentration and decreased transport coefficients essentially cancel at these conditions. There is a slight increase in the final conversion between 1 and 5 atmospheres, with essentially no further increase between 5 and 15 atmospheres.

The isolated effect of pressure alone on the carbonation kinetics can be deduced by comparing results at 15% CO_2 and 1 atmosphere to results at 1% CO_2 and 15 atmospheres. Since CO_2 concentration in the bulk gas is the same in these cases, the rate during the rapid reaction phase should be equal if transport resistances are unimportant. In contrast, if transport resistances are important the reduced transport coefficients at high pressure should result in a reduction in the global rate during the rapid reaction phase. Such results for sample 1 using 750°C calcination and carbonation temperatures are shown in Figure 31. Although the time delay for initiation of the reaction at high pressure somewhat complicates the comparison, it is clear that the rate in the rapid reaction phase is much higher at 1 atmosphere than at 15 atmospheres. Once again, however, there is relatively little difference in the final fractional conversions for the two runs.

Direct Comparison of the Three Base Sorbents

While results presented previously have shown the effect of various reaction parameters on the carbonation kinetics for each of the sorbents separately, no direct comparison of the performance of the three sorbents at equivalent reaction conditions has been presented. Such data are shown in Figure 32. Calcination conditions of 750°C, 1 atmosphere, in 100% N_2 , and carbonation conditions of 750°C, 1 atmosphere, in 15% CO_2 /85% N_2 were used in each test. Fractional carbonation is plotted against time for both the first and second cycles

Figure 31. The Effect of Pressure at Constant CO₂ Concentration: Sample 1.

Figure 32. Comparison of Carbonation Kinetics: Three Sorbents Through Two Cycles.

for each of the three sorbents. Within reasonable limits, the rate during the rapid reaction period is equal for each of the six carbonation tests. Important differences are associated with the fractional carbonation at the end of the rapid reaction phase, and the change in that quantity between the first and second cycles. In the first cycle, the end of the rapid reaction phase for sample 1 occurs at $X \sim 0.75$ while the comparable values for samples 7 and 9 are in the range of 0.85 to 0.9. By the end of the 70 minute carbonation period, the fractional carbonation of sample 1 increased to about 0.8, while both samples 7 and 9 reacted to greater than 90% completion. The decrease in reactivity between the first and second cycles was more severe for sample 1. At the end of the test, sample 1 experienced a decrease of about 14% between cycles, from $X \sim 0.8$ to $X \sim 0.69$, while the decrease for samples 7 and 9 was no more than 5%.

Although the absolute numbers change somewhat depending upon reaction conditions, the general trends exhibited by Figure 32 have been found to be rather consistent. There is relatively little difference in the rate during the rapid reaction period, but samples 7 and 9 consistently produce higher fractional carbonation levels and a smaller decrease in reactivity between cycles 1 and 2. The most significant exception to this general result is the unexpected decrease in second-cycle reactivity exhibited by samples 7 and 9 at 550°C carbonation temperature. This effect was illustrated by the data in Figure 28 and Table VIII.

TASK 4: DETAILED PARAMETRIC TESTS

In this task, one sorbent will be selected and a more detailed examination of the effects of calcination and carbonation reaction parameters will be conducted. In addition, small quantities of H_2S will be added in selected tests to examine the extent of the sulfidation reaction. Activities in this task are scheduled for year 02.

TASK 5: MULTICYCLE TESTS

The primary objective of this task, also scheduled during year 02, is to extend the number of cycles to which the sorbent is exposed to approximately 10, and to evaluate the sorbent performance in a synthetic coal gas containing CO, H₂, H₂O and (sometimes) H₂S as well as N₂ and CO₂.

TASK 6: STRUCTURAL PROPERTY MEASUREMENTS

The importance of sorbent structural properties in determining the kinetics of the carbonation reaction has been discussed in the literature review. A number of techniques to characterize the structure of the sorbents in various states have been, and will be, used throughout the project. During year 01 the techniques of primary emphasis have been mercury porosimetry to determine total pore volume and pore size distribution, and physical adsorption of methane to determine surface area using the BET method. The use of methane instead of the more common nitrogen for surface area determinations has been found to produce results having greater sensitivity and reliability for these relatively low surface area solids. During year 02, structural characterization techniques will be expanded to include scanning electron microscopy and helium pycnometry. The sorbents are being characterized in their as-received form, after calcination at various conditions, after carbonation at various conditions, and at selected stages of multiple calcination-carbonation cycles.

An overview of surface area and pore volume results for as-received and calcined samples is presented in Table IX. Surface area measurements have recently been plagued with instrument problems so that the surface area of sample 9 is not yet available. Neither surface area or pore volume results are available for sample 8 (calcium sulfate), and, because of the failure to obtain a usable sorbent from this sample, there are no plans at present to carry out such tests. The surface areas of the uncalcined (as-received) sorbents range from $0.4 \text{ m}^2/\text{g}$ for sample 1 to $11.8 \text{ m}^2/\text{g}$ for sample 3. Similarly, the pore volumes range from a low of $0.05 \text{ cm}^3/\text{g}$ for sample 1 to $0.48 \text{ cm}^3/\text{g}$ for sample 3. Pore

Table IX. Comparison of Surface Area and Pore Volume Results for
Calcium-Based Sorbents: Uncalcined and Calcined Forms

Sample	Uncalcined		Calcined ^(b)	
	BET Surface Area m ² /g	Pore Volume ^(a) cm ³ /g	BET Surface Area m ² /g	Pore Volume ^(a) cm ³ /g
1	0.4	0.05	15.0	0.17 ^(c)
2	4.5	0.31	8.2	0.50
3	11.8	0.48	3.8	0.53
4	1.6	0.09	14.1	0.25
5	4.0	0.33	2.5	0.44
6	8.7	0.43	4.6	0.51
7	3.3	0.25	8.9	0.95 ^(c)
8	NA	NA	NA	NA
9	NA	0.29	NA	0.41 ^(c)

(a) 0.003 to 4 micron diameter range

(b) Calcination temperature = 900°C

(c) Calcination time = 1 hr, calcination time somewhat variable in other tests.

volume is reported over a range of pore diameter diameters from 0.003 to 4.0 microns, with the upper limit being somewhat arbitrary. With powdered samples, it is impossible to distinguished between volume which is between the powder particles and true pore volume within a single particle. The cut-off diameter of 4 microns, while arbitrary, has been chosen in an effort to exclude the inter-particle volume component.

As shown in Table IX, calcination always results in an increase in pore volume while surface areas of the calcined sorbent both larger and smaller than those of the uncalcined precursor have been measured. Both the surface area and pore volume of the calcined sorbent are reported per unit mass of the original sorbent. In order to convert to the basis of unit mass of calcined product it is necessary to multiply by the ratio of the mass of the original precursor to the mass of the calcined sorbent. For sample 1 this ratio is $1.0/0.56 = 1.79$, so that the actual surface area and pore volume of calcined sample 1 are $26.8 \text{ cm}^2/\text{g}$ and $0.30 \text{ cm}^3/\text{g}$, respectively.

It is surprising that, although the structural properties of the carbonate samples (samples 1-6) in both the as-received and calcined forms are quite different, their carbonation behavior, as shown in Figures 18 and 19, was quite similar. It seems probable that impurities in the commercial products could be responsible for many of the observed differences in the structure of the carbonate samples. One common feature among samples 1-6 is that calcination produces a significant increase in pore volume, ranging from 0.03 to $0.12 \text{ cm}^3/\text{g CaCO}_3$, for pore diameters in the range of 0.02 to 0.2 microns. We conclude that these pores are found by CO_2 release during calcination. This is illustrated in Figure 33 where the cumulative volume versus pore diameter curves for as-received and calcined sample 1 are compared. In

Figure 33. Pore Size Distribution Before and After Calcination: Sample 1.

this example the incremental pore volume of $0.12 \text{ cm}^3/\text{g}$ is primarily in the diameter range of 0.03 to 0.06 microns. Sample 5 produced similar results with an increase in pore volume of $0.10 \text{ cm}^3/\text{g CaCO}_3$, primarily in the diameter range of 0.06 to 0.10 microns. Sample 3 provided an exception to the above general statement. Upon calcination, sample 9 (dolomite) exhibited an increase in pore volume which was similar to the other carbonate samples. The increase in pore volume was approximately $0.11 \text{ cm}^3/\text{g}$ dolomite and the majority of the pores formed were in the range of 0.03 to 0.06 microns diameter. Sample 7 (calcium acetate), in contrast, exhibited a much larger increase in pore volume and the pores formed were considerably larger, primarily in the range of 0.2 to 1.0 micron diameter.

The creation of pore volume during calcination along with subsequent changes which are caused by sintering and by the carbonation reaction have been examined in greater detail for the three base sorbents. Figure 34, for example, compares the pore size distribution for as-received and calcined sample 7 as a function of calcination temperature. Calcination was carried out for 1 hour in nitrogen at 1 atmosphere at the indicated temperature. The large increase in pore volume and the dominance of larger diameter pores are evident from this figure. More careful study also shows an incremental increase in pore volume in the vicinity of 0.04 micron diameter, similar to that shown in Figure 33 for sample 1. We attribute the formation of large pores to the loss of water of hydration and decomposition of the acetate group with the smaller increment at 0.04 microns diameter attributed to the decomposition of carbonate to oxide.

For practical purposes, it appears that the total pore volumes and pore size distributions are effectively the same following calcination

Figure 34. The Effect of Calcination Temperature on Pore Size Distribution: Sample 7.

at 750, 825, and 900°C. The latter temperature, however, appears to be near the limit as a significant change in size distribution and reduction in pore volume result at 1000°C calcination temperature. This result seems to be consistent with the tentative conclusion from kinetic tests that 900°C calcination temperature certainly should not be exceeded. Similar results were obtained when samples 1 and 9 were calcined at varying temperatures up to 1000°C.

The effect of calcination time at a constant calcination temperature of 900°C has been determined for samples 1, 7, and 9. Example results for sample 9 are shown in Figure 35. The decrease in pore volume associated with pores of greater than 0.1 micron diameter following calcination was unexpected, but appears to be real. The sharp increase in pore volume in the 0.03 to 0.06 micron range is similar to that observed for sample 1 (Figure 33). The distribution curves at various calcination times, while somewhat scattered, do not show any definite trends. Similar results have been obtained from samples 1 and 7. We conclude, therefore, that at 900°C, calcination time does not have an important effect on the pore structure of the sorbent.

Since calcination is effective in creating pore volume, it is logical to presume that subsequent carbonation would reduce or possibly eliminate the pore volume. Three tests, using each of the three base sorbents, in which calcination for 1 hour at 900°C and 1 atmosphere in nitrogen was followed by carbonation at 750°C and 1 atmosphere in 100% CO₂ have been completed. Pore size distribution curves for the as-received, calcined, and carbonated solids are shown in Figures 36, 37, and 38 for samples 1, 7, and 9, respectively.

For sample 1, we see from Figure 36 that the pore structure of the carbonated sorbent is very similar to that of the original CaCO₃. If

Figure 35. The Effect of Calcination Time on Pore Size Distribution: Sample 7.

Figure 36. Pore Size Distribution of Sample 1: As-Received, After Calcination, and After Carbonation.

Figure 37. Pore Size Distribution of Sample 7: As-Received, After Calcination, and After Carbonation.

Figure 38. Pore Size Distribution of Sample 9: As-Received, After Calcination, and After Carbonation.

any real difference exists, a slight decrease in pore volume is indicated. The very low pore volume of the sorbent after carbonation is consistent with the kinetic measurements which show that the carbonation reaction stops well short of completion. Once those pores in the 0.03 to 0.06 micron diameter range which are adjacent to the exterior of the particle are filled, further reaction becomes extremely slow as CO_2 must diffuse through the carbonate product layer. Note that the absence of pore volume from the porosimeter test does not imply that all pores have been filled. Isolated pores at the interior of the particle which are inaccessible to mercury may be present.

Four curves are shown in Figure 37 for sample 7. A partial calcination test was carried out at 600°C so that the water of hydration would be driven off and the acetate group would be decomposed leaving CaCO_3 . As shown in the figure, this step was responsible for creating most of the pore volume and most of the large diameter pores. Additional calcination at 900°C to drive off CO_2 and produce CaO actually resulted in a small decrease in total pore volume. However, small pores in the diameter range of 0.03 to 0.07 microns were formed in this step. Pores in this diameter range are consistent with CO_2 loss as shown by calcination of the other carbonate samples. Carbonation of sample 7 was essentially complete at these conditions, and a large reduction in pore volume occurred. However, a significant volume of open pores, primarily in the diameter range of 0.3 to 1.0 microns, remained. This too is consistent with the kinetic results.

Finally, Figure 38 shows that calcination of dolomite produces pores in the 0.04 to 0.08 micron diameter range and that subsequent carbonation of calcined dolomite fills only a portion of the pores. The premise that calcination of both MgCO_3 and CaCO_3 would be effective in

creating porosity and that the subsequent inert nature of the MgO would ease the pore closure problem seems to be verified.

Additional studies of pore volume and pore size distribution responses to different reaction conditions and to multicycle operation are planned.

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